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CHEMICAL EXAMINATION OF THE FRUITS OF *SOLANUM XANTHOCARPUM.*

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Received October 11, 1935.

Solanum xanthocarpum known as Bhoringani in Gujarati, Bhutkatya or Bhumiringani in Hindi, Kanteringani in Marathi, etc., is well known in Hindu Medicine, as its roots are one of the constituents of " Dashmul Ashava ". This plant grows abundantly in India in wild state. The stems are greenish grey with innumerable spines, and the flowers bright blue. The berries (fruits) are green when unripe and of different shades of yellow when ripe.[1]

The various parts of the plant are reputed in indigenous Hindu Medicine to have high medicinal value in various diseases like cough, asthma, fever, heart disease, etc.[2]

The plant under investigation belongs to the natural order *Solanacea*. Of the two classes of alkaloids which have been isolated from some of the plants belonging to this order one class gives alkaloids uncombined with sugars, such as atropine, hyoscyamine, hyoscine, etc., while the other class gives alkaloids combined with sugars and are known as gluco-alkaloids.

Dymock[3] states that the fruits of *Solanum xanthocarpum* were found on analysis to give alkaloidal reactions corresponding to solanine. The dried leaves gave 29·7% ash and contained a trace of an alkaloid, and an astringent acid giving a green precipitate with ferric chloride.

G. Pendse and S. Pendse[4] who have chemically examined the plant (including fruits) state that an alkaloid is present in very small quantities.

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[1] Kirtikar and Basu, *Indian Medicinal Plants*, part II, page 896.

[2] *Calcutta Med. Phys. Trans.*, 2, 406; Dymock's *Pharmacographia Indica*, 2, 557; Kirtikar and Basu, *Indian Medicinal Plants*, part II, p. 896.

[3] Dymock, *Pharmacographia Indica*, 2, 559.

[4] *Indian J. Med. Research*, 1932, 20, 663-670.

They attribute the physiological activity of the whole plant to potassium nitrate which is present in it to the extent of 1.6%.

The present authors have carried out a chemical examination of the fruits of *Solanum xanthocarpum* and isolated in the crystalline condition (1) the gluco-alkaloid $C_{44}H_{77}O_{19}N$, m.p. 288–89° C. (decomp.), which has been named " Solancarpine", (2) the alkaloid $C_{26}H_{43}O_3N$, m.p. 197–98° C. which has been named " Solancarpidine", and (3) the sterol $C_{36}H_{54}O_4$, m.p. 248° C. and named "Carpesterol". The products of hydrolysis of the gluco-alkaloid have been found to be the alkaloid (stated above), and the sugars glucose, rhamnose, and a hexose probably galactose. The hydrolysis of the gluco-alkaloid may probably be represented by the following equation :—

$$\underset{\text{gluco-alkaloid}}{C_{44}H_{77}O_{19}N} + H_2O = \underset{\substack{\text{aglucone}\\\text{(alkaloid)}}}{C_{26}H_{43}O_3N} + \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{galactose ?}}{C_6H_{12}O_6} + \underset{\text{rhamnose}}{C_6H_{12}O_5}$$

There is also obtained an inorganic salt which was identified as potassium chloride.

Experimental.

The fruits of the drug under investigation after digesting with Prollius' fluid and testing the resulting extract with usual alkaloidal reagents, indicated the presence of such a material. After preliminary experiments for working out the method of extraction, 40 lbs. of the dried ground material were successively extracted with petroleum ether and alcohol.

Alcoholic extract.—The extract on cooling deposited a white crystalline inorganic material, which was identified as potassium chloride. After removing this solid, the solvent was distilled off, when a dark coloured viscid extract was obtained, which was dried at 100° C. and finally in a desiccator over sulphuric acid.

A portion (200 grams) of the dried alcoholic extract was macerated with distilled water and kept overnight. It was then well stirred and allowed to stand for a few hours. The aqueous layer was then decanted and filtered. This operation was repeated with the solid left after decantation of the aqueous solution till no more was dissolved by water as judged from the colour of the solution. This gave an aqueous solution (A). The insoluble portion was then treated with cold 2% HCl solution till no more of it was dissolved by the acid. This gave an acid solution (B). The insoluble residue left after the acid treatment was dissolved in dilute sodium hydroxide solution, which gave the alkaline solution (C).

Aqueous solution (A).—This solution was clarified with neutral lead acetate. Excess of lead was removed by passing hydrogen sulphide gas in the solution.

The solution was then heated on a water-bath to remove hydrogen sulphide gas and precipitated with dilute ammonia. The precipitate was filtered, washed with a small bulk of water and dried. The dried solid was then dissolved in alcohol and the solution boiled with animal charcoal, filtered and kept for crystallisation. The separated white solid was recrystallised from the same solvent till the melting point was not further raised. The final product crystallised in the form of white, flat needles, which melted with decomposition at 288–89° C. Yield 19·4 grms., *i.e.*, 1·3% on the weight of the dried fruit.

Found : C, 56·93 ; H, 8·49 and N, 1·529. $C_{44}H_{77}O_{19}N$—requires C, 57·2 ; H, 8·34 and N, 1·51%.

The gluco-alkaloid is soluble in water and dilute acids. It is readily soluble in ethyl and methyl alcohols, moderately soluble in chloroform and acetone, and only sparingly soluble in benzene. With concentrated sulphuric acid it produces red colouration, which on keeping gradually turns blue, green and finally disappears. Concentrated nitric acid dissolves the substance on boiling producing a pink colour.

Acid hydrolysis of the gluco-alkaloid.—The substance (20 grms.) was heated with excess of 5% sulphuric acid under reflux on a boiling water-bath for about two to three hours. The separated solid was filtered, washed and dried. It was then powdered, decomposed with 20% ammonia, and extracted with ether. The ether extract was washed with water and dried over calcium chloride. Most of the solvent was then distilled off and the concentrated solution allowed to evaporate slowly, when a shining, white solid separated, which was crystallised from alcohol. It separated in the form of shining, white plate crystals, m.p. 197–98° C. Yield of the aglucone (alkaloid) 4·6 grms., *i.e.*, 0·3% on the weight of the dried fruits.

Found : C, 74·59 ; H, 10·39 and N, 3·37. $C_{28}H_{43}O_3N$ requires C, 74.82 H, 10·31 and N, 3·35%.

The alkaloid is soluble in hot ethyl and methyl alcohols, acetone, ethyl acetate, benzene and toluene. It is easily soluble in hot chloroform. With concentrated sulphuric acid it gives a reddish yellow colouration, which then changes to violet, and on addition of increasing proportion of water, to green, then yellow and finally disappears. With concentrated nitric acid it produces colouration similar to that of the gluco-alkaloid. The acid alcoholic solution of the substance gave tests for an alkaloid with the usual alkaloidal reagents.

The filtrate obtained from the acid hydrolysis of the gluco-alkaloid, after removing the solid, contained sugars which were identified by the

formation of their mixed osazones by (1) Perkin's method[5] and (2) their varying solubility in acetone. These experiments showed the presence of glucose, rhamnose, and another hexose, probably galactose.

The following salts of the alkaloid with different acids were prepared :—

(1) *Hydrochloride.*—A dilute solution of HCl was added to the solution of the alkaloid in acetone. The separated white solid was filtered, washed and crystallised from alcohol. White flat needle crystals, m.p. 313–14° C. (decomp.).

Found : Cl, (i) 7·58 and (ii) 7·65. $C_{26}H_{43}O_3N$–HCl requires 7·82 %.

(2) *Hydrobromide.*—This was prepared as (1) White flat needle crystals, m.p. 307–308° C. (decomp.).

Found : Br, (i) 15·71 and (ii) 15·94. $C_{26}H_{43}O_3N$–HBr requires 16·07 %.

(3) *Hydriodide.*—The alcoholic solution of the alkaloid was refluxed with a dilute solution of hydriodic acid for about 15 minutes. The resulting solution yielded white plate needles on slow evaporation of the solvent, m.p. 283–84° C. (decomp.).

Found : I, (i) 22·95 and (ii) 23·05. $C_{26}H_{43}O_3N$–HI requires 23·3%.

(4) *Sulphate.*—The alcoholic solution of the alkaloid was refluxed with a 5% alcoholic solution of sulphuric acid for about 5 minutes. The sulphate crystallised in shining white plate crystals, m.p. 293–94° C. (decomp.).

Found : N, 2·82. $C_{26}H_{43}O_3N$–HSO_4 requires N, 2·72%.

(5) *Nitrate.*—Prepared like (4). White needles, m.p. 271-72° C. (decomp.).

Found : N, 5·67. $C_{26}H_{43}O_3N$–HNO_3 requires 5·83%.

(6) *Acid oxalate.*—Prepared like (4). White needles, m.p. 238–39° C. (decomp.).

Found : N, 2·82. $C_{26}H_{43}O_3N$–HC_2O_4 requires 2·76%.

(7) *Acid tartarate.*—Prepared like (4). White needles, m.p. 224–25° C. (decomp.).

Found : N, 2·48. $C_{26}H_{43}O_3N$–$H_5C_4O_6$ requires 2·47%.

(8) *Picrate.*—The alcoholic solution of the alkaloid was refluxed with a concentrated alcoholic solution of picric acid for about 15 minutes. The picrate crystallised in long bright yellow needles, m.p. 148–49° C.

Found : N, 8·28. $C_{26}H_{43}O_3N$–$C_6H_3N_3O_7$ requires 8·66%.

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[5] *J.*, 1920, **97**, 1777.

The above described salts are moderately soluble in hot ethyl and methyl alcohols; soluble in traces in benzene, acetone and ethyl acetate. They are sparingly soluble in boiling water, and very sparingly soluble in boiling chloroform. They can be recovered from their solutions unchanged. The picrate was more soluble in benzene and chloroform than the other salts.

Decomposition of the salts by alkali.—All the salts described above, on decomposition with dilute alkalies, yielded the original alkaloid, m.p. 197–98° C. Its mixed melting point showed no depression.

Acid solution (B).—This solution gave the same alkaloid that was obtained from the aqueous solution on hydrolysis of the gluco-alkaloid.

Alkaline solution (C).—This solution on acidification gave a granular solid too small for further investigation.

Petroleum ether extract.—After the removal of the greater portion of the solvent the concentrated extract was kept aside for a day, when a crystalline white solid separated which was removed, and the extract further freed from the solvent by distilling under reduced pressure. This yielded an oil (about 4½ lbs.). The solid was recrystallised from alcohol. Shining white plate crystals, m.p. 248° C.

Found: C, 78·86 and H, 9·4. $C_{36}H_{54}O_4$ requires C, 78·54 and H, 9·81%.

This substance is soluble in boiling ethyl and methyl alcohols. Sparingly soluble in hot benzene, chloroform and acetone, but very sparingly soluble in petroleum ether. It gives characteristic colour tests of a sterol.

Acetylation.—0.5 grms. of the substance was heated with an excess of acetic anhydride for about one and half hour. It was then poured on crushed ice. A white solid separated after 3–4 hours, which was filtered, washed and recrystallised from alcohol. White silky needles, m.p. 193–94° C.

Found: C, 77·09 and H, 10·13. $C_{38}H_{56}O_5$ requires C, 77·03 and H, 9·5%.

This result shows the presence of at least one —OH group in the original compound.

Analysis of the ash.—A quantity (4·6 grms.) of the dried powder of the fruits was strongly heated in a platinum crucible. It left ash (0·28 grms. equal to 5·9%, and gave tests for K, Na, Mg, traces of Fe, Cl and CO_2).

Summary.

The material used in this investigation consisted of fresh fruits collected from Thana (near Bombay), and dried in air. The material was ground

and successively extracted with petroleum ether and alcohol. From the petroleum ether extract were obtained : (1) an oil, and (2) a sterol $C_{36}H_{54}O_4$, m.p. 248° C., designated "carpesterol". From the alcoholic extract were obtained : (1) a gluco-alkaloid $C_{44}H_{77}O_{19}N$, m.p. 288–89° C. (decomp.) named "solancarpine," (2) an alkaloid $C_{26}H_{43}O_3N$, m.p. 197–98° C. named "solancarpidine," (3) sugars : (i) glucose, (ii) rhamnose, and (iii) a hexose, probably galactose, and (4) an inorganic salt "potassium chloride".

One of us (I. Z. S.) takes this opportunity to express his sincere thanks to Principal Dr. T. S. Wheeler for his keen interest and valuable assistance.

PILLAI'S EXACT FORMULÆ FOR THE NUMBER $g(n)$ IN WARING'S PROBLEM.

By S. Chowla.
(*From the Government College, Lahore.*)

Received August 25, 1936.

1. Let n be a positive integer $\geqslant 7$; let $g(n)$ denote the least s such that every positive integer can be expressed as a sum of at most s non-negative nth powers. Denote by $[x]$ the greatest integer contained in x, by $\{x\}$ the fractional part of x. Write

$$l = [(\tfrac{3}{2})^n], \qquad j = [(\tfrac{4}{3})^n]$$

Pillai has recently proved the following remarkable results (1, 2):

Theorem 1: *If* $8 \leqslant \mathrm{n} \leqslant 30$, *then* $\mathrm{g(n)} = 2^n + l - 2$.

Theorem 2: *If* $\mathrm{n} \geqslant 30$ *and* $\{(\tfrac{3}{2})^n\} \leqslant 1 - \dfrac{l+3}{2^n}$, *then* $\mathrm{g(n)} = 2^n + (l-2)$.

When $\{(\tfrac{3}{2})^n\} > 1 - \dfrac{l+3}{2^n}$ (it seems not unlikely that this case never arises for $n \geqslant 8$) his previous results for $g(n)$ were not exact. Pillai has now found that

Theorem 3: *When* $\{(\tfrac{3}{2})^n\} \geqslant 1 - \dfrac{l-1}{2^n}$, *then*

(1) $g(n) = 2^n + l + j - 2$ if $\{(\tfrac{4}{3})^n\} \geqslant 1 - \dfrac{r}{3^n}$

(2) $g(n) = 2^n + l + j - 3$ if $\{(\tfrac{4}{3})^n\} < 1 - \dfrac{r}{3^n}$

where r *is defined by* $3^n = l \cdot 2^n + \mathrm{r}$.

The only cases in which an exact formula for $g(n)$ has not been obtained are, therefore,

(α) $3^n = l \cdot 2^n + 2^n - l - 2$.

(β) $3^n = l \cdot 2^n + 2^n - l - 1$.

(γ) $3^n = l \cdot 2^n + 2^n - l$.

When n is even, (α), (β) and (γ) are impossible. *Hence Pillai's theorems* 1, 2 *and* 3, *above determine* g(n) *exactly when* n *is even.*

Pillai also finds that

Theorem 4: $\mathrm{g(7)} = 143$

i.e., $g(n) = 2^n + (l - 2)$ *is also true for* $\mathrm{n} = 7$.

REFERENCE.

Pillai 1, "On Waring's Problem," *The Journal of the Annamalai University*, March 1936, 5, No. 2, 145—166.

Pillai 2, "On Waring's Problem," *Journal of the Indian Math. Society*, New Series, 2, No. 1, 16—44.

THE VISIBILITY OF ULTRASONIC WAVES AND ITS PERIODIC VARIATIONS.

By N. S. Nagendra Nath.
(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received August 20, 1936.

1. Introduction.

That ultrasonic waves travelling in a medium may be observed directly with suitable optical arrangements has been shown by Hiedemann, Bachem, Asbach and Hoesch[1] at Köln. Their method consists in observing through a microscope a beam of light which emerges from a rectangular cell containing supersonic waves which travel perpendicular to the direction of the propagation of the incident light. If the supersonic waves are progressive, a Kerr cell is also needed. Since supersonic waves are present in the medium they create periodic fluctuations in its density and consequently its optical properties. If light passes through such a medium, one should naturally expect periodic changes in the intensity of light on the emerging wave front. The wave-length of the periodic intensity fluctuation will be equal to the wave-length of the supersonic waves. However, in the case of standing waves, the wave-length corresponding to the fluctuations of the *average* intensity of light with respect to time will be half of the wave-length of the supersonic waves. This method has been used to determine the ultrasonic velocities in transparent solids and liquids.

Recently Raman and Nath[2] pointed out, in these *Proceedings*, the theoretical basis of the observability of supersonic waves in general terms based on their general theory of the propagation of light in a medium containing supersonic waves. Later, Pisharoty[3] developed the theory of the visibility of ultrasonic waves basing his investigation on Raman-Naths' preliminary theory. He obtained the very interesting result that even a periodic corrugated beam of light having initially a constant intensity will, during its propagation, develop into a periodic corrugated beam with periodic intensity changes on it. This means that if a microscope be used for observing the emerging beam, periodic intensity changes can be seen on the beam when the microscope is not exactly focussed on the emerging face of the

[1] *Zeits. f. Phy.*, **87**, 734, 738; **88**, 395; **89**, 502; **90**, 322; **96**, 268; **98**, 141.
[2] C. V. Raman and N. S. Nagendra Nath, *Proc. Ind. Acad. Sci.*, 1936, **3**, 459.
[3] P. R. Pisharoty, *Proc. Ind. Acad. Sci.*, 1936, **4**, 27.

cell where there are no intensity changes. He also pointed out that if the microscope be continuously focussed away from the emerging face, any particular form of the intensity grating can be seen exactly at distances which are integral multiples of a definite length. But Pisharoty's paper is marred by some errors.

The purpose of this paper is to develop the general theory of the visibility of ultrasonic waves and to show that the periodic visibility is characteristic of any general periodic supersonic wave. The above fact in a special case was first pointed out by Pisharoty. Special cases have also been worked out here and diagrams are drawn to illustrate the theoretical results.

2. *The Propagation of Light in a Medium filled with Sound Waves.*

The partial differential equation governing the propagation of light in a medium with time-variation and space-variation in its refractive index is

$$\nabla^2 \psi = \left[\frac{\mu\,(x, y, z, t)}{c}\right]^2 \frac{\partial^2 \psi}{\partial t^2} \quad .. \quad .. \quad .. \quad .. \quad (1)$$

if the frequency of the time-variation of $\mu\,(x, y, z, t)$ is very slow compared to the time variation of the wave-function of light. This is indeed so in the problem we are considering for the time-variation of $\mu\,(x, y, z, t)$ corresponds to the frequency of the sound waves which is negligible compared to the frequency of light.

The dependence of ψ on y can be ignored if we choose the axes of reference such that the x-axis points to the direction of the propagation of the plane sound waves and the z-axis points to the direction of propagation of the incident plane wave of light.

Considering now that $\mu\,(x, t)$ varies slowly in time compared to $\exp\,[2\pi i\nu t]$, where ν is the frequency of the incident light, we can write ψ as given by

$$\exp\,[2\pi i\nu t]\ \phi\,(x, z, t) \quad .. \quad .. \quad .. \quad .. \quad (2)$$

where ϕ varies slowly in time compared to $\exp\,[2\pi i\nu t]$. On the consideration that $\nu^* << \nu$ where ν^* denotes the frequency of the sound waves we can show that

$$\left|\, 4\pi\nu \frac{\partial \phi}{\partial t} \right| << |\, 4\pi^2\nu^2\phi \,| \text{ and } \left|\frac{\partial^2 \phi}{\partial t^2}\right| << |\, 4\pi^2\nu^2\phi \,| \;.. \quad .. \quad (3)$$

Substituting (2) in (1) and using (3), we get the equation for ϕ as

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\{\mu\,(x, t)\}^2 \phi \;.. \quad .. \quad .. \quad .. \quad (4)$$

and we may get ψ by the equation (2).

The form of the wave-front in the medium.—If we imagine a translation of the cell by an integral multiple of the wave-length of the sound waves along the x-axis, the experimental conditions will remain unchanged. This symmetry of the experiment demands that ϕ is some general periodic function of x, *i.e.*,

$$\phi\,(x+p\lambda^*, z, t) = \phi\,(x, z, t) \quad .. \quad .. \quad .. \quad .. \quad (5)$$

where p is an integer. Since the experimental conditions also repeat themselves after a time q/ν^* where q is an integer, ϕ is also periodic in time with the period $1/\nu^*$, *i.e.*,

$$\phi\,(x, z, t + q/\nu^*) = \phi\,(x, z, t) \quad .. \quad .. \quad .. \quad .. \quad (6)$$

where q is an integer.

Conditions (5) and (6) enable us to write the double Fourier expansion of ϕ as given by

$$\phi\,(x, z, t) = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{r,s}\, e^{2\pi irx/\lambda^*}\, e^{2\pi is\nu^* t} \quad .. \quad .. \quad .. \quad (7)$$

Progressive sound waves.—In the case of progressive sound waves travelling along the positive direction of the x-axis, we have the property that the form and position of the wave obtained by a translation of the cell along the x-axis by $\rho\lambda^*$ where ρ is any number is the same as those of the wave which had appeared at a time ρ/ν^* earlier.

This condition can be put analytically as

$$\phi\,(x + \rho\lambda^*, z, t) = \phi\,(x, z, t - \rho/\nu^*) \quad .. \quad .. \quad .. \quad (8)$$

Using (8) in (7), we get

$$\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{r,s}\,(z)\, e^{2\pi irx/\lambda^*}\, e^{2\pi is\nu^* t}\, e^{2\pi ir\rho}$$

$$= \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{r,s}\,(z)\, e^{2\pi irx/\lambda^*}\, e^{2\pi is\nu^* t}\, e^{-2\pi is\rho} \quad .. \quad .. \quad (9)$$

Comparing the Fourier coefficients on each side of (9), we get

$$f_{r,s}\,(z)\, e^{2\pi ir\rho} = f_{r,s}\,(z)\, e^{-2\pi is\rho} \quad .. \quad .. \quad .. \quad .. \quad (10)$$

where ρ is any number. (10) can only be true if

$$f_{r,s}\,(z) = 0 \qquad \text{when } r \neq -s \quad .. \quad .. \quad .. \quad .. \quad (11)$$

The condition (11) restricts the number of terms in the Fourier expansion of ϕ given by (7), so that

$$\phi\,(x, z, t) = \sum_{-\infty}^{\infty} f_r\,(z)\, e^{2\pi irx/\lambda^*}\, e^{-2\pi ir\nu^* t} \quad .. \quad .. \quad .. \quad (12)$$

Standing sound waves.—In the case of standing sound waves, we have the property that the form and position of the wave obtained by a translation

of the cell along the x-axis by $p\lambda^*/2$ where p is an integer, is the same as those of the wave which would appear at a time $p/2\nu^*$ after or at the same time earlier. By this condition, ϕ obeys the property

$$\phi\,(x + \frac{p\lambda^*}{2}, z, t) = \phi\left(x, z, t \pm \frac{p}{2\nu^*}\right) \quad .. \quad .. \quad .. \quad (13)$$

where p is an integer. Using (13) in (7), we get

$$\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{r,s}\,(z)\, e^{2\pi irx/\lambda^*}\, e^{2\pi isv^*t}\, e^{\pi irp}$$

$$= \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{r,s}\,(z)\, e^{2\pi irx/\lambda^*}\, e^{2\pi isv^*t}\, e^{\pm\pi isp} \quad .. \quad .. \quad (14)$$

Comparing the Fourier coefficients on each side of (14), we get

$$f_{r,s}\,(z)\, e^{\pi irp} = f_{r,s}\,(z)\, e^{\pi isp} \quad .. \quad .. \quad .. \quad .. \quad (15)$$

where p is an integer. (15) can only be true if r and s are both even integers or odd integers. Thus the Fourier expansion of ϕ can be written as given by

$$\phi\,(x, z, t) = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{2r,2s}\,(z)\, e^{2\pi i2rx/\lambda^*}\, e^{2\pi i2sv^*t}$$

$$+ \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{2r+1,\,2s+1}\,(z)\, e^{2\pi i\overline{2r+1}x/\lambda^*}\, e^{2\pi i\overline{2s+1}v^*t} \quad .. \quad (16)$$

The wave-front at the emerging face of the cell.—Since the boundary of the emerging face is given by $z = L$, where L is the length of the cell along the z-axis, the wave-front at $z = L$ will be

$$\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{r,s}\,(L)\, e^{2\pi irx/\lambda^*}\, e^{2\pi isv^*t} \quad .. \quad .. \quad .. \quad .. \quad (17)$$

If we only change the origin of the axes of reference to $(0, L)$, we will have to write the above as

$$\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} a_{r,s}\, e^{2\pi irx/\lambda^*}\, e^{2\pi isv^*t} \quad .. \quad .. \quad .. \quad .. \quad (18)$$

where

$$a_{r,s} = f_{r,s}\,(0) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (19)$$

3. *Propagation of a Periodic Corrugated Wave in a Homogeneous Medium like Air.*

Let us consider the propagation of light whose initial wave-front at $z = 0$ is given by

$$\exp\,[2\pi i\nu t]\,\Phi\,(x, 0, t)$$

where

$$\Phi\,(x, 0, t) = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} a_{r,s}\, e^{2\pi irx/\lambda}\, e^{2\pi isv^*t} \quad .. \quad .. \quad .. \quad (20)$$

The symmetry of the initial wave-front demands that the form of the propagated wave should also be periodic in λ^* along the x-axis and in time with the period $1/\nu^*$. Thus the propagated wave is of the form

$$\Phi = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} g_{r,s}(z)\, e^{2\pi i r x/\lambda^*}\, e^{2\pi i s \nu^* t} \quad .. \quad .. \quad .. \quad (21)$$

such that

$$g_{r,s}(0) = a_{r,s} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (22)$$

satisfying the boundary conditions. Φ satisfies the equation

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\Phi \quad .. \quad .. \quad .. \quad .. \quad (23)$$

taking the refrative index of the medium as unity. Substituting (21) in (23) and comparing the Fourier coefficients on each side of (23), we get

$$\frac{d^2 g_{r,s}}{dz^2} + \frac{4\pi^2}{\lambda^2}\left(1 - \frac{r^2\lambda^2}{\lambda^{*2}}\right) g_{r,s} = 0 \quad .. \quad .. \quad .. \quad (24)$$

Since we are only interested in the propagation of light to the right of the x-axis, the solution for $g_{r,s}$ is given by

$$g_{r,s}(z) = a_{r,s}\, e^{-\frac{2\pi i z}{\lambda}\sqrt{\left(1 - \frac{r^2\lambda^2}{\lambda^{*2}}\right)}} \quad .. \quad .. \quad .. \quad (25)$$

so that the propagated wave ψ is of the form given by

$$\Psi = e^{2\pi i \nu t}\,\Phi$$

$$= \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} a_{r,s}\, e^{2\pi i\left[(\nu + s\nu^*)t - \frac{z\cos\theta_r - x\sin\theta_r}{\lambda}\right]} \quad .. \quad .. \quad (26)$$

where

$$\sin\theta_r = \frac{r\lambda}{\lambda^*} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (27)$$

Each of the component terms in (26) represents a wave of constant amplitude $a_{r,s}$ propagated in the direction whose z- and x-direction cosines are $\cos\theta_r$ and $-\sin\theta_r$ respectively. From the analysis of the wave given in (26) it should not be inferred that a superposition of a set of plane waves of constant amplitudes would also lead to a wave of constant amplitude. Indeed such a wave possesses, in general, an amplitude grating on it, *i.e.*, the amplitude on the wave-front will be a general periodic function of x. The intensity on the wave-front given by (26) is given by

$$|\Phi|^2 = \Phi\Phi^{\dagger} = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} g_{r,s}\, g^{\dagger}_{u,v}\, e^{2\pi i(r-u)x/\lambda^*}\, e^{2\pi i(s-v)\nu^* t} \quad (28)$$

Putting $r - u = l$ and $s - v = m$, we get

$$|\Phi|^2 = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} g_{r,s}\, g^{\dagger}_{r-l,\, s-m}\, e^{2\pi i l x/\lambda^*}\, e^{2\pi i m \nu^* t}$$

$$= \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} B_{l,m}\, e^{2\pi i l x/\lambda^*}\, e^{2\pi i m \nu^* t} \quad .. \quad .. \quad .. \quad (29)$$

where

$$B_{l,m} = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} g_{r,s}\, g^{\dagger}_{r-l,\, s-m}$$

$$= \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} a_{r,s}\, a^{\dagger}_{r-l,\, s-m}\, e^{-\frac{2\pi i z}{\lambda}} \left[\sqrt{\left(1-\frac{r^2\lambda^2}{\lambda^{*2}}\right)} - \sqrt{\left(1-\frac{(r-l)^2\lambda^2}{\lambda^{*2}}\right)}\right] \quad (30)$$

Let us suppose that λ/λ^* is small such that higher powers of it than λ^2/λ^{*2} are negligible in the index of the exponential term. This will be so under the experimental conditions. The first term having an influence in the exponential term is of the order $\lambda z/\lambda^{*2}$ and the next term is of the order $\lambda^3 z/\lambda^{*4}$. The influence of the second term is practically zero under the experimental conditions employed. With this consideration we can write $B_{l,m}$ as given by

$$B_{l,m} = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} a_{r,s}\, a_{r-l,\, s-m}\, e^{\frac{\pi i z}{\lambda}\left[\frac{r^2\lambda^2}{\lambda^{*2}} - \frac{(r-l)^2\lambda^2}{\lambda^{*2}}\right]}$$

$$= \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} a_{r,s}\, a^{\dagger}_{r-l,\, s-m}\, e^{-\pi i \lambda z l\,(l-2r)/\lambda^{*2}} \quad .. \quad .. \quad (31)$$

By the help of (31) we can write $\Phi\Phi^{\dagger}$ as given by

$$\Phi\Phi^{\dagger} = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} a_{r,s}\, a^{\dagger}_{r-l,\, s-m}\, e^{2\pi i l x/\lambda^*}\, e^{2\pi i m \nu^* t}\, e^{-\pi i \lambda z l\,(l-2r)/\lambda^{*2}} \quad (32)$$

(32) shows that the intensity grating on the wave-front along the x-axis with the period λ^* repeats itself during its propagation with a definite period along the z-axis. This can be easily seen if one substitutes for z

$$z + \frac{2k\lambda^{*2}}{\lambda} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (33)$$

where k is an integer. From this it follows that

$$|\Phi(x, z, t)|^2 = \left|\Phi\left(x, z + \frac{2k\lambda^{*2}}{\lambda}, t\right)\right| \quad .. \quad .. \quad .. \quad (34)$$

So, we can say that the intensity grating on the wave-front at z is exactly the same as that on the one at $z + \frac{2k\lambda^{*2}}{\lambda}$. That is, the intensity grating on the wave-front repeats itself along the z-axis with the period $2\lambda^{*2}/\lambda$.†

† For $\lambda^* = 0{\cdot}1$ cm., and $\lambda = 5 \times 10^{-5}$ cm., the period is 400 cm. while for $\lambda^* = 0{\cdot}01$ cm., and for the same wave-length of light, the period is 4 cm.

Progressive corrugation.—We will now consider as a particular case of the above, that of a progressive corrugation on the wave-front at the boundary. According to (11)

$$a_{r,s} = 0 \qquad \text{for } r \neq -s \quad .. \quad .. \quad .. \quad .. \quad (35)$$

Thus

$$|\Phi|^2 = \sum_{-\infty}^{\infty} B_l \, e^{2\pi i l x/\lambda^*} \, e^{-2\pi i l \nu^* t} \quad .. \quad .. \quad .. \quad (36)$$

where

$$B_l = \sum_{-\infty}^{\infty} a_r \, a^\dagger_{r-l} \, e^{-\pi i z l \, (l-2r)\lambda/\lambda^{*2}} \quad .. \quad .. \quad .. \quad (37)$$

The average intensity with respect to time on the wave-front is

$$\frac{1}{2\pi} \int_0^{2\pi} \Phi \, \Phi^\dagger d\epsilon \quad .. \quad .. \quad .. \quad .. \quad .. \quad (38)$$

where $\epsilon = 2\pi\nu^* t$. This is of course constant on the wave-front given by B_0 which is $\Sigma a_r \, a^\dagger_r$. The intensity on the wave-front, at any instant, is given by (36) and (37) which shows that the intensity grating on the wave-front at z is the same as the grating on the wave-fronts at $z + 2k\lambda^{*2}/\lambda$ where k is a positive integer. Conditions may be such that any particular form of the grating may have a lower period than $2\lambda^{*2}/\lambda$. For example, suppose the initial values a's are such that

$$\sum_{r=-\infty}^{\infty} a_r \, a^\dagger_{r-l} = 0 \qquad l \neq 0 \quad .. \quad .. \quad .. \quad .. \quad (39)$$

From (37) and (39) one can see that

$$B_l \, (x, 0, t) = \sum_{r=-\infty}^{\infty} a_r \, a^\dagger_{r-l} = 0 \qquad l \neq 0 \quad .. \quad .. \quad (40)$$

and

$$B_0 \, (x, 0, t) = \Sigma \, a_r \, a^\dagger_r \quad .. \quad .. \quad .. \quad .. \quad (41)$$

Thus

$$|\Phi \, (x, 0, t)|^2 = \sum_{-\infty}^{\infty} a_r \, a^\dagger_r \quad .. \quad .. \quad .. \quad .. \quad (42)$$

which means that the intensity is constant on the wave-front at $z = 0$. The constant intensity on the wave-front has a lower period in z than $2\lambda^{*2}/\lambda$ for

$$B_l \, (x, z, t) = e^{-\pi i z l^2 \lambda/\lambda^{*2}} \, \Sigma \, a_r \, a^\dagger_{r-l} \, e^{2\pi i z \lambda r/\lambda^{*2}}$$

so that

$$B_l \left(x, \frac{k\lambda^{*2}}{\lambda}, t\right) = e^{-\pi i k l^2} \, \Sigma \, a_r \, a^\dagger_{r-l} = 0 \qquad l \neq 0 \quad .. \quad (43)$$

where k is an integer. Thus we can say that if the propagated wave has at any z a constant intensity on the wave-front, it will have the same on all those wave-fronts at distances differing from z by an integral multiple of λ^{*2}/λ.

Stationary corrugation.—In this case

$$\Phi = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} g_{r,s}(z)\, e^{2\pi i r x/\lambda^*}\, e^{2\pi i s \nu^* t} \quad .. \quad .. \quad .. \quad (44)$$

where r *and* s *are both even integers or odd integers* and

$$g_{r,s}(z) = a_{r,s}\, e^{-\frac{2\pi i z}{\lambda}\sqrt{\left(1-\frac{r^2\lambda^2}{\lambda^{*2}}\right)}} \quad .. \quad .. \quad .. \quad (45)$$

The intensity on the wave-front is given by

$$\Phi\,\Phi\dagger = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} g_{r,s}\, g\dagger_{r-l,\ s-m}\, e^{2\pi i l x/\lambda^*}\, e^{2\pi i m \nu^* t} \quad .. \quad (46)$$

where r *and* s *or* l *and* m *are both even integers or odd integers.* The *average intensity* on the wave-front is

$$\mathrm{I}(x, z) = \frac{1}{2\pi}\int_0^{2\pi} \Phi\,\Phi\dagger\, d\epsilon \quad .. \quad .. \quad .. \quad .. \quad (47)$$

where $\epsilon = 2\pi\nu^* t$

From (47) and (46) we find

$$\mathrm{I}(x, z) = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} g_{r,s}\, g\dagger_{r-l,s}\, e^{2\pi i l x/\lambda^*} \quad .. \quad .. \quad .. \quad (48)$$

where l *should be an even integer.* This is so for the right-hand side expression in (48) is the constant term in (46) for $m = 0$, which is an even integer so that l corresponding to $m = 0$ is also an even integer. In view of this consideration, we can change l to $2m$ where the m may be any integer. Hence

$$\mathrm{I}(x, z) = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} g_{r,s}\, g\dagger_{r-2m,s}\, e^{4\pi i m x/\lambda^*}$$

$$= \sum_{-\infty}^{\infty} \mathrm{B}_{2m}\, e^{2\pi i 2 m x/\lambda^*} \quad .. \quad .. \quad .. \quad .. \quad (49)$$

where

$$\mathrm{B}_{2m} = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} a_{r,s}\, a\dagger_{r-2m,s}\, e^{-4\pi i \lambda z m(m-r)\lambda/\lambda^{*2}} \quad .. \quad .. \quad (50)$$

From (50), one can easily see that

$$\mathrm{B}_{2m}(x, z) = \mathrm{B}_{2m}(x, z + k\,\lambda^{*2}/2\lambda) \quad .. \quad .. \quad .. \quad (51)$$

where k is an integer. This means that the *average intensity* grating on the wave-front at z repeats itself at all distances differing from the original one by an integral multiple of the distance $\lambda^{*2}/2\lambda$.

4. *Special Cases.*

We will consider in this section two special cases. The wave-front at the boundary is considered to have no intensity variations on it.

A special case of progressive fluctuation.—Let

$$a_r = \mathrm{J}_r(v) \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (52)$$

where v is a constant and $\mathrm{J}_r(v)$ is the Bessel function of the rth order. The wave at the boundary is

$$\Phi(x, 0, t) = \sum_{-\infty}^{\infty} \mathrm{J}_r(v)\, e^{2\pi i r x/\lambda^*}\, e^{-2\pi i r \nu^* t} \quad .. \quad .. \quad .. \quad (53)$$

It can be easily seen that the wave (53) has no intensity grating on it for

$$|\Phi(x, 0, t)|^2 = \Sigma\ \mathrm{B}^0_l\, e^{2\pi i l x/\lambda}\, e^{-2\pi i l \nu^* t} \quad .. \quad .. \quad .. \quad (54)$$

where

$$\begin{aligned}\mathrm{B}^0_l &= \sum_{r=-\infty}^{\infty} \mathrm{J}_r(v)\, \mathrm{J}_{r-l}(v) \\ &= \sum_{r=-\infty}^{\infty} \mathrm{J}_r(v)\, \mathrm{J}_{l-r}(-v) \\ &= \mathrm{J}_l(0) = 0 \qquad \text{if } l \neq 0 \\ &= 1 \quad \text{if } l = 0 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (55)\end{aligned}$$

Hence

$$|\Phi(x, 0, t)|^2 = 1 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (56)$$

which shows that the intensity is constant on the wave-front at $z = 0$.

Putting $z = h\lambda^{*2}/\lambda$, we get*

$$\begin{aligned}\Phi(x, h\lambda^{*2}/\lambda, t) &= \sum_{-\infty}^{\infty} \mathrm{J}_r(v)\, e^{2\pi i r x/\lambda^*}\, e^{-2\pi i r \nu^* t}\, e^{\pi i r^2 h} \\ &= \sum_{-\infty}^{\infty} \mathrm{J}_{2r}(v)\, e^{2\pi i 2r x/\lambda^*}\, e^{-2\pi i 2r \nu^* t}\, e^{4\pi i r^2 h} \\ &\quad + \sum_{-\infty}^{\infty} \mathrm{J}_{2r+1}(v)\, e^{2\pi i \overline{2r+1} x/\lambda^*}\, e^{-2\pi i \overline{2r+1} \nu^* t}\, e^{\pi i (2r+1)^2 h} \quad (57)\end{aligned}$$

(*i*) Suppose $h = \frac{1}{4}$. Then

$$\begin{aligned}\Phi(x, \lambda^{*2}/4\lambda, t) &= \sum_{-\infty}^{\infty} \mathrm{J}_{2r}(v)\, e^{2\pi i 2r x/\lambda^*}\, e^{\pi i r^2}\, e^{-2\pi i 2r \nu^* t} \\ &\quad + \sum_{-\infty}^{\infty} \mathrm{J}_{2r+1}(v)\, e^{2\pi i \overline{2r+1} x/\lambda^*}\, e^{\pi i (r^2+r+\frac{1}{4})}\, e^{-2\pi i \overline{2r+1} \nu^* t} \\ &= 2 \sum_{0}^{\infty}{}' (-)^r \mathrm{J}_{2r}(v) \cos\left[2\pi 2r\, (x/\lambda^* - \nu^* t)\right] \\ &\quad + 2ie^{\pi i/4} \sum_{0}^{\infty} \mathrm{J}_{2r+1}(v) \sin\left[2\pi\, (2r+1)\, \{x/\lambda^* - \nu^* t\}\right] \\ &= \cos\left(v \cos 2\pi \overline{x/\lambda^* - \nu^* t}\right) + ie^{\pi i/4} \sin\left(v \sin 2\pi \overline{x/\lambda^* - \nu^* t}\right).\end{aligned}$$

* The constant factor $\exp[2\pi i z/\lambda]$ is omitted in Φ which does not give intensity changes.

Hence

$$|\Phi\ (x,\ \lambda^{*2}/4\lambda,\ 0)\ |^2 =$$
$$\cos^2\ (v\ \cos\ bx) + \sin^2\ (v\ \sin\ bx) - \sqrt{2}\ \cos\ (v\ \cos\ bx) \sin\ (v\ \sin\ bx) \quad (58)$$

(*ii*) Also.

$$|\Phi\ (x,\ \lambda^{*2}/4\lambda,\ 0)\ |^2 = |\Phi\ (x,\ 3\lambda^{*2}/4\lambda,\ 0)\ |^2 \quad .. \quad .. \quad (59)$$

(*iii*) Suppose $h = \frac{1}{2}$. Then

$$|\Phi\ (x,\ \lambda^{*2}/2\lambda,\ 0)\ |^2 = 1 - \sin\ (2v\ \sin\ bx) \quad .. \quad .. \quad (60)$$

(*iv*) $$|\Phi\ (x,\ 3\lambda^{*2}/2\lambda,\ 0)\ |^2 = 1 + \sin\ (2v\ \sin\ bx) \quad .. \quad .. \quad (61)$$

This example clearly shows that a wave initially having a constant intensity on it will develop itself, during its propagation, into one having an intensity grating on it. The constant intensity on the wave-front will be of course repeating with the period λ^{*2}/λ along the z-axis.

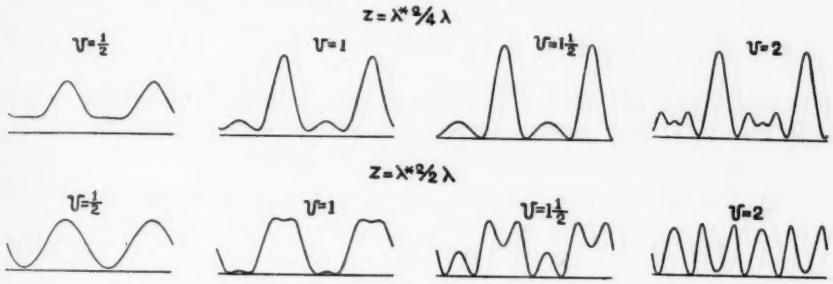

FIG. 1.

A special case of standing fluctuation.—The form for Φ in the case of a standing fluctuation* is

$$\Phi = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} a_{r,s}\ e^{2\pi i r x/\lambda^*}\ e^{2\pi i s \nu^* t}\ e^{\pi i z r^2 \lambda/\lambda^{*2}} \quad .. \quad .. \quad (62)$$

where r *and* s *are both even integers or odd integers.* Let us write

$$b_r\ (t) = \sum_{s=-\infty}^{\infty} a_{r,s}\ e^{2\pi i s \nu^* t} \quad .. \quad .. \quad .. \quad .. \quad (63)$$

Let us choose b's such that each of them is given by[4]

$$b_r\ (t) = \mathrm{J}_r\ (v\ \sin\ 2\pi\nu^* t) \quad .. \quad .. \quad .. \quad .. \quad (64)$$

where v is some constant.

Thus

$$\Phi = \sum_{-\infty}^{\infty} \mathrm{J}_r\ (v\ \sin\ \epsilon)\ e^{2\pi i r x/\lambda^*}\ e^{\pi i z r^2 \lambda/\lambda^{*2}} \quad .. \quad .. \quad .. \quad (65)$$

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* The constant factor exp $(-2\pi i z/\lambda)$ is omitted as it does not create any intensity changes.

[4] C. V. Raman and N. S. Nagendra Nath, *Proc. Ind. Acad. Sci.*, 1936, **3**, 75.

So

$$|\Phi|^2 = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} J_r(v \sin\epsilon)\, J_{r-l}(v \sin\epsilon)\, e^{2\pi i l x/\lambda^*}\, e^{-\pi i z l \lambda (l-2r)/\lambda^{*2}} \quad (66)$$

The *average intensity with respect to time* is given by

$$I(x, z) = \frac{1}{2\pi} \int_0^{2\pi} |\Phi|^2 \, d\epsilon$$

$$= \frac{1}{2\pi} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \int_0^{2\pi} J_r(v \sin\epsilon)\, J_{r-l}(v \sin\epsilon)\, d\epsilon\, e^{2\pi i l x/\lambda^*} \times e^{-\pi i z l \lambda (l-2r)/\lambda^{*2}} \quad (67)$$

One can easily find that all integrals in (67) in which l is odd vanish. Thus

$$I(x, z) = \frac{1}{2\pi} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} C_{r,2l}\, e^{\pi 4 i l x/\lambda^*}\, e^{-4\pi i z l (l-r)\lambda/\lambda^{*2}} \quad (68)$$

where

$$C_{r,2l} = \int_0^{2\pi} J_r(v \sin\epsilon)\, J_{r-2l}(v \sin\epsilon)\, d\epsilon \quad (69)$$

(68) shows that the average intensity grating is periodic along the x-axis with the period $\lambda^*/2$ and that any particular form of the intensity grating will repeat itself along the z-axis with the period $\lambda^{*2}/2\lambda$.

(i) The intensity is constant on the wave-front at the boundary $z = 0$ for

$$I(x, 0) = \frac{1}{2\pi} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} C_{r,2l}\, e^{4\pi i l x/\lambda^*} \quad (70)$$

where

$$\sum_r C_{r,2l} = \int_0^{2\pi} \sum_{r=-\infty}^{\infty} J_r(v \sin\epsilon)\, J_{r-2l}(v \sin\epsilon)\, d\epsilon$$

$$= \int_0^{2\pi} \sum_{r=-\infty}^{\infty} J_r(v \sin\epsilon)\, J_{2l-r}(-v \sin\epsilon)\, d\epsilon$$

$$= 0 \text{ if } l \neq 0$$

$$= 2\pi \text{ if } l = 0 \quad (71)$$

so that

$$I(x, 0) = 1 \quad (72)$$

which shows that the intensity is constant on the wave-front at the boundary.

(ii) Suppose $z = \lambda^{*2}/4\lambda$. Then

$$I(x, \lambda^{*2}/4\lambda) = \frac{1}{2\pi} \sum_{-\infty}^{\infty} B_{2l}\, e^{4\pi i l x/\lambda^*} \quad (73)$$

where

$$B_{2l} = e^{-\pi i l^2} \sum_{r=-\infty}^{\infty} C_{r,2l}\, e^{\pi i l r}$$

(*a*) Suppose l is even. Then

$$B_{4m} = \Sigma\, C_{r,4m} = \int_0^{2\pi} \sum_{-\infty}^{\infty} J_r\,(v \sin \epsilon)\, J_{4m-r}\,(-v \sin \epsilon)\, d\epsilon$$

$$= 0 \text{ if } m \neq 0$$

$$= 2\pi \text{ if } m = 0 \qquad .. \qquad .. \qquad .. \qquad (74)$$

(*b*) Suppose l is odd. Then

$$B_{2(2m+1)} = \Sigma(-)^{r+1}\, C_{r,2(2m+1)}$$

$$= -\int_0^{2\pi} \sum_{r=-\infty}^{\infty} J_r\,(v \sin \epsilon)\, J_{2(2m+1)-r}\,(v \sin \epsilon)$$

$$= -\int_0^{2\pi} J_{2(2m+1)}\,(2v \sin \epsilon)\, d\epsilon$$

$$= -4\int_0^{\pi/2} J_{2(2m+1)}\,(2\,v \sin \epsilon)\, d\epsilon$$

$$= -2\pi\, J_{(2m+1)^2}\,(v) \qquad .. \qquad .. \qquad .. \qquad .. \qquad (75)$$

Thus

$$I\,(x,\lambda^{*2}/4\lambda) = 1 - \sum_{l=-\infty}^{\infty} J_{(2l+1)^2}\,(v)\, e^{4\pi i\,(2l+1)\,x/\lambda^*}$$

$$= 1 - 2\sum_{l=0}^{\infty} J_{(2l+1)^2}\,(v) \cos\,[4\pi\,(2l+1)x/\lambda^*]$$

This example clearly shows quantitatively the development of an intensity grating on a wave which had a standing corrugation on it but had constant intensity on it initially. Fig. 2 shows diagrammatically the intensity gratings for some values of v.

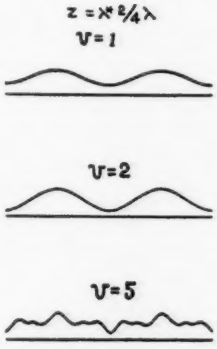

FIG. 2.

These figures give an interpretation of the pictures of the intensity gratings obtained by Bär,[5] who has obtained a multiplicity of the fringes under suitable experimental conditions.

5. *Summary.*

The general theory of the visibility of ultrasonic waves has been developed. The theory shows that the intensity grating on a *general periodic corrugated* (*both amplitude and phase*) wave-front of light will repeat itself on all those at distances from the original one by integral multiples $2\lambda^{*2}/\lambda$, where λ^* is the wave-length of the corrugation and λ is the wave-length of light. Special cases have been worked out to illustrate the theoretical results. These theoretical results await experimental confirmation.

The author is grateful to Prof. C. V. Raman for the discussions on this subject.

[5] R. Bär, *Helv. Phy. Acta.*, 1935, **8**, 591 ; 1936, **9**, 265.

DISTRIBUTION OF TEMPERATURE AND VAPOUR PRESSURE IN THE NEIGHBOURHOOD OF A WATER-SURFACE.

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Abstract.

The present paper describes the results of experiments made in the laboratory to determine the distribution of temperature and vapour pressure in the neighbourhood of an evaporating water-surface with wind speeds varying from 0 to $2\frac{1}{2}$ metres per second. Fine dry and wet thermo-couples were used to determine the temperatures. It was noticed that when the water-surface was warmer than air, there were conspicuous fluctuations of temperature above the water-surface, the maximum fluctuations being at a height of about 1 cm. above the surface. A table is given showing the heights above the surface at which the temperature and vapour pressure changes amounted to one-half the total changes.

The water-vapour content in the air of an ordinary closed room remains sensibly constant for short intervals of time. If there is an exposed surface of water, the air immediately above the water-surface becomes saturated, exerting the maximum vapour pressure corresponding to the surface temperature of the water. When the room air is not saturated, there would be a rapid decrease of vapour pressure as we move away from the water-surface reaching the steady room value beyond a certain distance from the surface. In the presence of wind, the layer in which the rapid change of humidity occurs may be expected to become thinner.

The existence of a laminary boundary layer is generally assumed in dealing with problems of heat or moisture exchange between the ground and the atmosphere. The average thickness of this layer over a smooth snow-surface has been computed by H. Sverdrup[1] in the following way. The transport of heat between 4 cm. and 100 cm. above the surface was calculated from the values of eddy-conductivity and temperature-gradient deduced from observations of wind and temperature at different heights. This flux of heat was equated to the flux across the boundary layer at the surface. Using the equation

$$Q = \lambda \frac{\Delta \theta}{\Delta z}$$

where λ is the heat conductivity of the air, $\Delta\theta$ the difference of temperature between the surface and the top of the boundary layer and Δz the thickness of the boundary layer, Δz was calculated. From temperature observations, Sverdrup found the value of Δz to be ·08 cm. and from humidity observations, found it to be 0·13 cm. Calculating Δz from Wüst's observations over the sea, Sverdrup obtained 0·03 cm. and 0·09 cm. from temperature and humidity observations respectively. Brunt[2] from theoretical considerations suggests a relation of the following form

$$\delta = \frac{60}{V}$$

where δ is the thickness of the boundary-layer in cm. and V is the wind velocity in cm. per second.

Messrs. S. L. Malurkar and L. A. Ramdas[3] studied the distribution of temperature over ground heated by insolation in calm weather. Their results showed a rapidly decreasing lapse-rate of temperature with height in a layer of depth 10 to 15 cm. above ground, after which the rate of fall became comparatively small.

In the present paper, an account is given of some measurements made in the laboratory of the distribution of temperature and moisture in the neighbourhood of an evaporating surface of water, both when the water-surface was warmer than the surrounding air and when it was colder.

Apparatus.—The water was contained in an elliptical bath-tub with diameters about 3 ft. and 2 ft. It was filled with fresh tap-water up to the brim. Wet and dry thermo-couples were used for measuring the temperature and vapour pressure. The thermo-couples were made of thin copper-constantan wires and the wet thermo-couple was kept moist by winding round it loosely spun cotton thread with its free end dipping into a beaker of distilled water. The thermo-couples were mounted in the same horizontal line on a ⌐¬-shaped glass frame at a distance of about 2 cm. from each other, a stretched silk thread being used to keep them in position. A third thermocouple was used for finding the temperature of the water-surface. The three couples had a common junction dipping into water contained in a vacuum flask.

By means of a simple mechanical arrangement, the whole glass-frame could be raised or lowered and the height of the couples above the surface of water read with the aid of a vertical glass scale and an adjustable pointer. To produce a current of air, an electric fan was used and the wind speed could be changed by altering the current through it or changing its distance from the water-surface. The height of the fan and its position were so adjusted that the flow of wind was as nearly as possible parallel to the surface.

The wind velocity was measured at a height of 3 to 4 inches above the water-surface with a small Fuess air-meter in the earlier experiments and with a kata-thermometer later. The temperature and humidity of the air in the room were determined by observations with an Assmann psychrometer.

There was no difficulty in keeping the water-surface at a lower temperature than that of the air, as evaporation itself lowers it. For raising the temperature, an electric heating element consisting of wire stretched over a wooden frame was used at the bottom of the tub. A preliminary survey of the temperature all over the surface was made to see if the temperature was uniform. The observations at different heights were made either in ascending or descending order of heights. Apjohn and August's formula (see Kaye and Laby's *Table of Constants*) was used for calculating the vapour pressures, the value of the constant A being taken to be 0·0008.

Results.

(1) *Water-surface cooler than air; no wind* (Table I and Fig. 1).—The peculiarities of the distributions of vapour pressure and temperature in this case are: the vapour pressure decreases with height, rapidly at first and more slowly later, and practically the whole change takes place within 5 cm. of

TABLE I.

Temperature and Vapour Pressure at different heights above water-surface.

Water temperature .. 26°·55 C.
Room temperature.. .. 27°·6 C.
Room humidity 75%
No wind.

Height above surface cm.	Temperature °C. D.B.	W.B.	Vapour pressure mm.
0·1	26·6	26·4	25·6
0·2	26·7	26·3	25·3
0·3	26·7	26·2	25·1
0·4	26·8	26·1	24·9
0·8	26·9	25·7	24·1
1·2	26·9	25·4	23·4
1·6	27·0	25·0	22·6
2·0	27·1	24·7	22·0
2·4	27·1	24·5	21·6
2·8	27·1	24·4	21·4
3·5	27·2	24·1	20·8
4·0	27·4	24·1	20·7
5·0	27·4	24·1	20·5
10·0	27·4	24·0	20·5

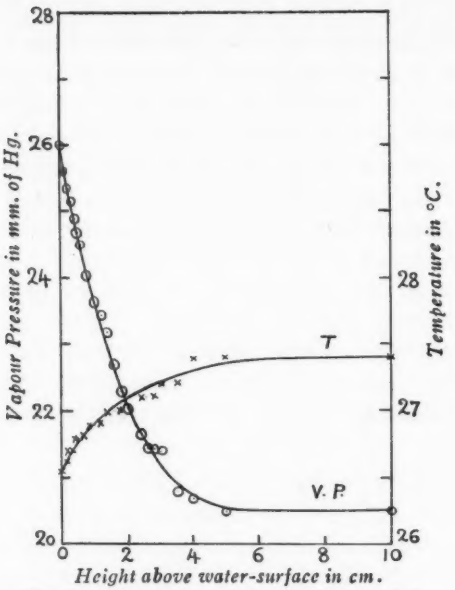

FIG. 1. Water-surface cooler than air ; no wind.

the water-surface. The temperature increases with height and changes more or less conversely to vapour-pressure.

(2) *Water-surface cooler than air ; with wind* (Table II, Fig. 2).—Fig. 2 represents the conditions where there was a wind velocity of 234 cm./sec.

TABLE II.

Temperature and Vapour Pressure at different heights above water-surface.

Water temperature .. 23°·2 C.
Room temperature.. .. 26°·7 C.
Room humidity 47%
Wind—234 cm./sec.

Height above surface cm.	Temperature °C. D.B.	W.B.	Vapour pressure mm.
0·2	25·6	20·0	14·6
0·3	25·8	19·7	14·0
0·4	25·9	19·7	14·0
0·5	26·2	19·5	13·5
0·7	26·3	19·5	13·5
1·0	26·3	19·4	13·3
1·5	26·3	19·3	13·2
2·0	26·5	19·3	13·1
3·0	26·6	19·3	13·0
5·0	26·6	19·2	12·9

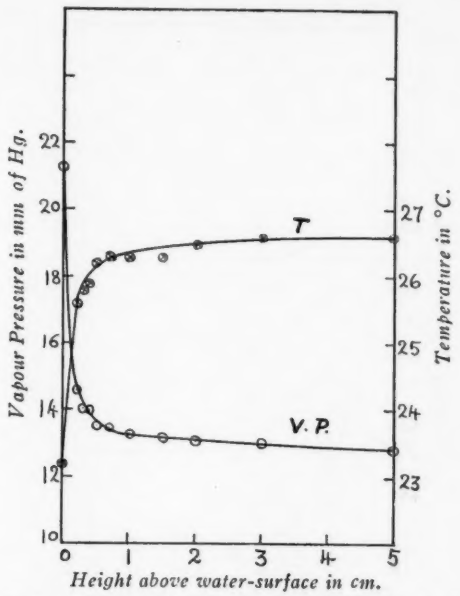

FIG. 2. Water-surface cooler than air ; Wind 234 cm./sec.

at a height of 4 inches above the water-surface. The curves are similar to those obtained with no wind, but the thickness of the layer over which the changes take place is only about 1 cm.

(3) *Water-surface warmer than air ; no wind* (Fig. 3).—There does not seem to be any essential difference between this case and the first, except that the change becomes small after about 2 cm. distance from the water-surface. This may be expected from the fact that the air layer near the water-surface would be less stable when the water is warmer than the air.

Some interesting effects were observed in this case. Both dry and wet bulb temperatures showed considerable fluctuations at any fixed height within the first few centimetres above the surface. The values plotted in Fig. 3 are means of a number of observations at each height. Fig. 4 shows graphically the fluctuations of temperature at different heights above the surface in a particular case. At different levels above the surface, the standard deviations of temperature were calculated and it was found that the deviation was a maximum at a distance of about 1 cm. from the surface and that it fell down on either side of it. This interesting feature is to be explained by the fact that above a thin layer, the exchange of energy takes place through the medium of small eddies carrying heat and moisture upward

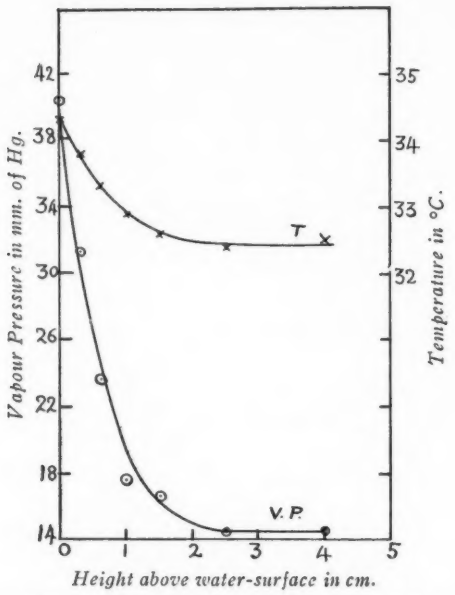

FIG. 3. Water-surface warmer than air; no wind.

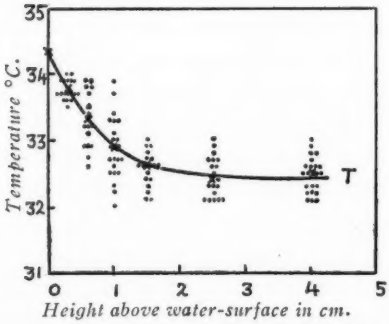

FIG. 4. Fluctuations of temperature at different heights above water-surface when water was warmer than air.

and bringing down cooler and drier air from above; these eddies are continually in movement over the surface and that the maximum fluctuations of temperature take place near the lower limit of height to which these eddies reach. Another interesting peculiarity which is more difficult to understand was that the dry-bulb temperature near this height some times showed temperatures distinctly below that of the room.

(4) *Water-surface warmer than air ; with wind.*—Fig. 5 shows distributions of temperature and vapour pressure when the water-surface was warmer

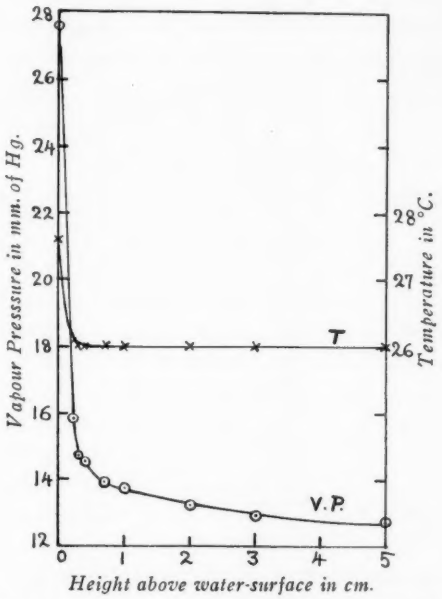

FIG. 5. Water-surface warmer than air; wind 203 cm./sec.

than air and there was a wind with speed of about 2 metres/sec. parallel to the water-surface. The results are similar to those in Fig. 2.

Thickness of the boundary layer.—Since the outer boundary of the laminary layer is not definite and the variation of temperature or vapour pressure within it is not uniform, we have to adopt some working definition of its thickness. Adopting the convention that the thickness within which the surface value of temperature or vapour pressure undergoes half the total change gives a measure of the thickness δ of the laminary layer, I have tabulated in Table III the thickness δ obtained from different sets of observations. There is a tendency for δ from vapour pressure observations to be slightly smaller than that from temperature observations, but the difference is not decisive. The values of δ obtained with higher wind velocities show that under ordinary open air conditions, it may be expected to be 0·10 to 0·15 cm. When there is wind, it does not appear to make any appreciable difference whether the air is cooler or warmer than air, but in calm, the thickness of the layer is definitely smaller when the water is warmer.

TABLE III.

Thickness of the air layer near the boundary within which half the total change of temperature or vapour-pressure takes place.

Temperature difference water—air	Wind velocity cm./sec.	δ in cm.	
		From temperature observations	From vapour pressure observations
Negative	0	1·78	1·12
,,	56	0·35	0·37
,,	64	0·35	0·20
,,	70	0·20	0·20
,,	100	0·20	0·15
,,	113	0·30	0·20
,,	162	0·30	0·23
,,	197	0·12	0·12
,,	203	0·17	0·13
,,	234	0·13	0·11
Positive	0	0·39	0·55
,,	100	0·20	0·18
,,	203	0·10	0·15

Conclusion.

Experiments similar to the above have also been made in the open air, but the work requires extension and it is hoped to present the results in a later paper.

I am thankful to Dr. K. R. Ramanathan for suggesting the above investigation and for his helpful advice during its progress. The experiments were performed in the Physical Laboratory of the Fergusson College, Poona, and my thanks are due to Profs. Joshi and Barave for providing me the necessary facilities for the work.

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1. H. U. Sverdrup, "The Eddy Conductivity of the air over a smooth snow field," *Geofys. Publ.*, Oslo, **9**, No. 7.
2. D. Brunt, *Physical and Dynamical Meteorology*, 1934, p. 262.
3. S. L. Malurkar and L. A. Ramdas, "High Lapse-rates of temperature very near the ground," *Ind. Jour. Phys.*, 1931, **6**, 495.

STUDIES IN THE CONESSINE SERIES.

Part II. Relationship between N-Stability and Pharmocological Action of Conessine and Iso-Conessine.

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In more recent years a striking connection has been observed between the pharmacological activity of some nitrogenous compounds on the one hand and the N-stability of radicals attached to the basic nitrogen on the other. Thus the substitution of the methyl radical in choline and codeine by allyl and other β-γ unsaturated radicals, whose N-stability has been noted in the course of an exhaustive study by von Braun and co-workers[1] to decrease proportionately with the degree of unsaturation, causes an intrinsic change in the pharmacological action of these alkaloids. This change has been very carefully studied in the case of codeine derivatives by von Braum and co-workers[2] who have established that the substitution of methyl by allyl in its molecule reverses the inhibitory action of codeine on respiration, and that similar but qualitatively weaker action, than is noted in case of allyl nor-codeine, appears when the $-C=C-$ bond in the allyl is replaced by some other unsaturated centre.

The isolation and easy synthesis of a series of N-demethylated bases in the conessine series[3] tempted one of us who had taken part in the above investigations,[4] to synthesise the allyl and other unsaturated derivatives of the nor-bases of conessine and study the change in the pharmacological action of conessine occasioned by these substitutions of its methyl groups. The preparation of these derivatives presented such difficulties, that this project had to be given up for the present. When, however, iso-conessine was obtained by one of us[5] and shown to be definitely more potent than conessine

[1] *Ber.*, 1902, **35**, 1279,

[2] *Ber.*, 1926, **59**, 1081, and preceding papers.

[3] S. Siddiqui, *J. Ind. Chem. Soc.*, 1934, 283; S. Siddiqui and R. H. Siddiqui, *ibid.*, 1931, 539.

[4] S. Siddiqui, *Dissertation*, Frankfurt/M, 1927.

[5] *Proc. Ind. Acad. Sci.*, 1935, 426.

in its inhibitory action on the respiration of frogs, it appeared of great interest to investigate in what manner the isomerisation had affected the N-stability of the methyl groups in the molecule on the one hand, and the N-stability of the conessine radical itself on the other. The former feature was tested through the action of BrCN, whereby it was noted that the N-stability of the methyl groups in iso-conessine is definitely less than in case of conessine in so far as the action of BrCN on iso-conessine, leading to cyano-nor-iso-conessine was much more energetic than the corresponding reaction in case of conessine, and the removal of the second methyl group from the monocyanated product took place within an hour of mixing the components in ethereal solution as against nearly a whole week required for the completion of the reaction

$$2\ C_{23}H_{37}N_2.CN + BrCN = C_{22}H_{34}N_2 : (CN)_2 + C_{23}H_{37}N_2.CN.CH_3Br$$

in the conessine series (*loc. cit.*). For testing the comparative N-stability of conessine and iso-conessine radicals ($C_{21}H_{31}\geq$) the ease with which the Hoffmann's Abbau took place in the two molecules was made the criterion. Here it was found that, iso-conessine is recovered in almost theoretical yield on heating iso-conessine dimethyl ammonium hydroxide, two molecules of methyl alcohol being apparently split off. In case of conessine, apoconessine was obtained as reported by Kanga, Aiyyar and Simonson[6] and corroborated by Spaeth[7] and Hromatka, but conessine also could be isolated to the extent of about 15 % from the mixture of degradation products. The partial splitting of CH_3OH, estimated by Spaeth and Hromatka (*loc. cit.*) must have been due to this and the second uncrystallised base, which both Simonson and Spaeth (*loc. cit.*) noted in working up the degradation products, must have contained conessine, which crystallises with difficulty when impure. Polstorff and Schirmer[8] had also obtained conessine through Hoffmann's Abbau of the base, and it appears they were not quite as wrong in this finding as Spaeth and Hromatka summarily supposed them to be.

The dimethoiodides and dimethochlorides of both conessine and iso-conessine behaved in a similar manner on dry distillation *in vacuo*, yielding back in each case the tertiary bases conessine and iso-conessine. Also, attempts at reductive degradation of the quaternary ammonium chloride with the help of (5%) Sodium amalgum after Emde proved fruitless in both the cases, dimethyl-ammonium-chlorides of conessine and iso-conessine being recovered unchanged.

It thus appears that both conessine and iso-conessine radicals are characterised by a high degree of N-stability. There is sufficient evidence, however,

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[6] *J. Chem. Soc.*, 1926, 2123.
[7] *Ber.*, 1930, **63**, 126.
[8] *Ber.*, 1886, **19**, 78.

in the comparative behaviour of the two bases towards BrCN and Hoffmann's Abbau to show that the accentuation of the pharmacological action noted in iso-conessine has been occasioned by changes in the nucleus of conessine which have decreased the N-stability of the methyl groups and correspondingly increased that of its own nucleus.

It has been shown at the outset that the decrease in the N-stability of the radical substituted for methyl in the codeine molecule produced a reversal in the pharmacological action. In the conessine series just the contrary has happened. The pharmacological action has intensified. Thus, while it appears that the exact direction of the change occasioned by the alteration of the N-stability of the radicals attached to the basic nitrogen cannot be predetermined, the results of the present investigations along with the studies in the codeine derivatives discussed above, do lead to the conclusion that the intensity and character of the pharmacological action is very largely dependent on this factor.

Experimental.

Action of cyanogen bromide on iso-conessine.—1·9 g. (1 mol) of BrCN (freshly prepared after Scholl)[9] in 20 c.c. ether were slowly added to a solution of 6·5 g. (1 mol) iso-conessine in 30 c.c. ether with good cooling and stirring. The cream coloured crystalline precipitate which immediately separated was filtered off and washed well with ether and ethyl acetate. The crystals, which proved to be a mixture of iso-conessine di-methobromide and iso-conessine hydrobromide, were dissolved in the aqueous washings of the ethereal filtrate. The aqueous solution was made strongly ammoniacal and shaken out with ether. The base from the ethereal layer was identified with iso-conessine, through its optical activity and the mixed melting points of its hydroiodide and picrate. The aqueous, ammoniacal layer was treated with caustic soda and shaken out with chloroform. The residue from the dried chloroform layer gave after purification through methyl alcohol and ether a white crystalline powder melting at 316° and giving no depression on admixture with iso-conessine di-methobromide. The original, ethereal filtrate from the BrCN reaction products was shaken out with 10 % acetic acid, and the bright yellow acetic acid solution made alkaline with caustic soda. The treacly precipitate which settled down crystallised on cooling and on recrystallisation from ether melted at 116–117°. The yield of pure cyano-iso-nor-iso-conessine thus obtained was 3·5 g. (95 % of theory). The ethereal layer, from which the cyanated base had been shaken out with

[9] *Ber.*, 1896, **29**, 1822.

acetic acid, yielded a treacly product which failed to crystallise out and was presumably impure dicyano-iso-conimine.

Heating or the substitution of chlroform or ethyl acetate for ether as a solvent for this reaction lowered the yield of cyano-iso-nor-conessine and produced undefinable, reddish, neutral products.

Action of cyanogen bromide on cyano-iso-nor-iso-conessine.—1 g. of cyano-iso-nor-iso-conessine in 20 c.c. dry ethyl acetate was treated with a solution of 0·3 g. BrCN in 10 c.c. dry ethyl acetate and the mixture kept at room temperature. Thin silky plates of cyano-iso-nor-iso-conessine hydrobromide (m.p. 269–70°) soon began to separate out and the reaction was found to be complete in about 2 hours. The filtrate from the crystalline mass (0·4 g.) was successively washed with acetic acid, dilute alkali and water and dried over sodium sulphate. The treacle left on removal of the solvent was dissolved in ether, when on slow evaporation dicyano-iso-conimine was obtained as snow-white prismatic rods (m.p. 132–33°).

Characterisation of the products of BrCN reaction.—Cyano-iso-nor-iso-conessine :—It is sparingly soluble in petroleum ether, readily soluble in other usual organic solvents. From absolute alcohol it crystallises in large rectangular, prismatic plates melting at 116–17°. [Found : CH_3, 8·1; $C_{23}H_{37}N_2.CN$ requires (for $2N\text{-}CH_3)CH_3$, 8·2 %.]

——*hydrochloride* was obtained by adding ethereal hydrochloric acid to a solution of the base in ethyl acetate and ether as snow-white aggregates of needles. Recrystallised from a mixture of alcohol, acetone and ether, it melted at 259–60°. It is soluble in alcohol and water, difficultly soluble in acetone, insoluble in ether. [Found : after drying in air, Cl, 17·2 ; after drying *in vacuo* at 100°, Cl, 14·7 ; after further drying *in vacuo* at 120°, Cl, 13·5 ; $C_{23}H_{37}N_2.CN.HCl + 1\frac{1}{2}$ HCl requires Cl, 19·4 ; $C_{23}H_{37}N_2.CN.HCl +$ HCl requires Cl, 16·1 ; $C_{23}H_{37}N_2.CN.HCl + \frac{1}{2}$ HCl requires Cl, 12·6 %.]

The hydrochloride apparently crystallises with $1\frac{1}{2}$ HCl. Of this nearly 1 HCl is removed on drying *in vacuo* at 120° and $\frac{1}{2}$ HCl appears to be more closely attached to the molecule. Chlorine estimation in the corresponding salt of the conessine series, cyano-iso-conessimine hydrochloride, showed that this also crystallises with $1\frac{1}{2}$ HCl which, however, it loses entirely on heating *in vacuo* at 100°. [Found : after drying over P_2O_5, 19·9 ; after drying to constant weight at 100°, Cl, 9·09 ; $C_{23}H_{37}N_2.CN.HCl$ requires Cl, 8·79 %.][10]

——*chloroplatinate* was obtained as a cream coloured semi-crystalline powder sparingly soluble in hot water, fairly soluble in alcohol, and melting

[10] *J. Indian Chem. Soc.*, 1934, 11, 787.

at 210–15° (decom.). [Found : Cl, 18·4 ; Pt, 16·9 ; $(C_{23}H_{37}N_2.CN.HCl)_2PtCl_4$ requires Cl, 18·6 ; Pt, 17·1 %.]

——*aurichloride* formed a cream-coloured powder, soluble in alcohol and insoluble in cold water. It stuck to the sides at 100° and melted with frothing at 190°.

——*hydrobromide.* As isolated from the reaction products of BrCN and cyano-iso-nor-iso-conessine, it formed white thin shining plates, soluble in alcohol and water and melting at 269–70°. On treating with ammonia it yielded cyano-iso-nor-iso-conessine, as proved by its mixed melting point with a pure sample of the cyno base. [Found : after drying at 100°, Br, 19·0 ; CH_3, 7·2 ; $C_{23}H_{37}N_2.CN.HBr$ requires Br, 17·9 ; (for 2 N-CH_3) CH_3, 6·7 %.] As shown above in the case of the corresponding hydrochloride, the hydrobromide also appears to crystallise with HBr of crystallisation which was not completely removed at 100°, thus giving 1·1 % too high Br.

The corresponding reaction product in the conessine series was considered to be the methobromide on the basis of its N and Br values (*loc. cit*). [Found : N, 8·7 ; Br, 16·7 ; $C_{23}H_{37}N_2.CN.CH_3Br$ requires N, 9·1 ; Br, 17·3 ; $C_{23}H_{37}N_2.CN.HBr$ requires Br, 17·9 ; N, 9·4 %.] Its N.CH_3 value, determined now, showed this also to be the hydrobromide, as was further proved by its yielding the cyno base. [Found : CH_3, 7·3 ; $C_{23}H_{37}N_2.CN.HBr$ requires CH_3 (for 2N–CH_3), 6·7 ; $C_{23}H_{37}N_2.CN.CH_3$ Br requires (for 3CH_3) CH_3, 9·7 %.]

——*picrate* was obtained as a bright yellow crystalline powder soluble in alcohol and very sparingly soluble in water. It shrank at 169°, and melted at 173–75°.

Iso-conessine dimethobromide. It is easily soluble in alcohol, chloroform and water and melted at 316°, giving a depression of 10° in admixture with conessine dimethobromide. From its aqueous solution it is precipitated with caustic soda and can be shaken out with chloroform. [Found : CH_3, 13·9 %; $C_{24}H_{40}N_2.(CH_3.Br)_2$ requires (for 5 N–CH_3) CH_3, 13·7 %.]

Dicyano-iso-conimine. It is readily soluble in alcohol, chloroform, ethyl acetate, sparingly in ether and petroleum ether, and melts at 132–33°. Being neutral in character, it does not form any salts and is insoluble in acids and alkalies. [Found : CH_3, 4·7 %; $C_{22}H_{34}N_2.(CN)_2$ requires (for 1 N–CH_3) CH_3, 4·0 %.]

Saponification of cyano-iso-nor-iso-conessine.—1 g. of cyano-iso-nor-iso-conessine in 5 c.c. absolute alcohol with 15 c.c. of 20% absolute alcoholic potash were refluxed on the water-bath for 30 hours. A crystalline mass slowly separated out, which was identified as potassium carbonate. The

reddish residue left on removal of the major portion of the solvent was extracted with ether. The base from the ethereal extract was taken up in dilute acetic acid, charcoaled and treated with a concentrated solution of potassium iodide. On recrystallising the white crystalline hydroiodide from water pure iso-nor-iso-conessine hydroiodide (0·5 g.) was obtained. It melted at 292–93° and gave no depression in m.p. on admixture with the hydroiodide of the base, obtained through direct isomerisation of iso-conessimine. The residual base from the hydroiodide filtrate gave a picrate and a hydrochloride showing no depression in their mixed melting points with the corresponding salts of iso-nor-iso-conessine.

The base from the pure hydroiodide showed $[\alpha]_D^{40°} = +100·5°$; iso-conessine, $[\alpha]_D^{35°} = +101°$.

Saponification of iso-dicyano conimine.—1 g. dicyano-isoconimine saponified and worked up in a similar manner as the mono-cyano product yielded 0·64 g. iso-conimine dihydroiodide, m.p. 320°. On treatment with caustic soda the filtrate from the hydroiodide yielded a further quantity of iso-conimine as free base. The base from the pure hydroiodide gave with ethereal HCl a hydrochloride, which melted at 336–37° (decomp.), gave no depression with iso-conimine hydrochloride, and showed $[\alpha]_D^{39} = +69·5°$ in 1% absolute alcoholic solution.

Hoffmann's Abbau of Iso-Conessine.

Iso-conessine dimethyl ammonium hydroxide.—Iso-conessine dimethiodide obtained by adding 6·7 g. (4 mols) methyl iodide in 20 c.c. acetone to a solution of 4·3 g. (1 mol) iso-conessine in 100 c.c. acetone, m.p. 330–34° [Found: CH_3, 12·4 ; $C_{24}H_{40}N_2.(CH_3I)_2$ requires (for 5-NCH_3) CH_3, 11·7 %], was treated in aqueous solution with freshly precipitated silver oxide. On evaporation of the filtrate from the above on the water-bath, a reddish coloured residue was obtained which crystallised in broom-like aggregates of flat needles which were extremely hygroscopic.

——*picrate* was obtained from the components in aqueous solution as brilliant yellow aggregates of needles, insoluble in water, sparingly soluble in alcohol, m.p. 220°.

——*chloride* was obtained by treating the iodide with freshly precipitated silver chloride on the water-bath. It was very hygroscopic and formed a white powder when dry, m.p. 297–98°.

——*chloroplatinate* was obtained as aggregates of buff coloured prismatic rods melting at 259°. [Found : Pt, 24·6 ; $(C_{24}H_{40}N_2.2\ CH_3Cl).PtCl_4$ requires Pt, 24·6 %.]

Dry distillation of iso-conessine dimethyl ammonium hydroxide.—2 g. of quaternary base were heated at 200° in a metal bath. The resultant reddish molten mass dissolved in petroleum ether and yielded a crystalline hydrochloride (1 g.) melting at 309° (parallel iso-conessine HCl, m.p. 313°). It showed $[\alpha]_D^{40°} = +71°$ as against $[\alpha]_D^{36°} = +72°$ noted for iso-conessine hydrochloride, both in 1% solution. The chloroplatinate from the above hydrochloride formed long prismatic rods (m.p. 267–69°)—Iso-conessine chloroplat, m.p. 271–73°. [Found: Pt, 25·4%; $(C_{24}H_{40}N_2 \cdot 2HCl)\ PtCl_4$ requires Pt, 25·4 %.] The mother liquors from the hydrochloride yielded 0·3 g. iso-conessine hydroiodide (m.p. 321°).

Dry distillation of iso-conessine dimethyl ammonium chloride.—0·9 g. of the chloride (m.p. 298°) was heated at 310°/4 mm. when it distilled over completely. The distillate was soluble in petroleum ether and was found to be iso-conessine through the m.p. and optical activity ($[\alpha]_D^{40°} = +63°$) of its hydroiodide. Heated slowly at ordinary pressure, iso-conessine dimethochloride began to darken from 150° and appeared to resinify on further heating. On quick heating over a free flame it melted with frothing to a light reddish liquid which hardened on cooling, was entirely soluble in petroleum ether and was found to be iso-conessine through the m.p. and activity of its hydroiodide.

Hoffmann's Abbau of Conessine.

Conessine dimethyl ammonium hydroxide—Conessine dimethiodide was first obtained by adding methyliodide (10·5 g.; 4 mols) to a petroleum ether solution of conessine (6·4 g.; 1 mol) as white silky rectangular plates (9·5 g.), melting at 300–301°. The aqueous solution of the methiodide was treated with freshly precipitated silver hydroxide and the filtrate evaporated on the water-bath to dryness when the ammonium base was obtained as a reddish treackly residue.

——*picrate*, formed stout prismatic rods, m.p. 260° (decomp.).

——*chloride* was prepared in the same manner as the corresponding iso-conessine salt. Crystallised from alcohol, acetone and ethyl acetate, it formed brooms and stars of needles, m.p. 284° (decomp.), $[\alpha]_D^{37°} = +15°$.

——*cholroplatinate* of the ammonium base was obtained as an orange coloured mass of closely packed needles. It is insoluble in alcohol and water and melted at 247° (blackening and decomp.). [Found: Pt, 24·6; $C_{24}H_{40}N_2 \cdot 2CH_3Cl$. $PtCl_4$ requires Pt, 24·6 %.]

Dry distillation of conessine dimethyl ammonium hydroxide.—The ammonium base was carefully heated with a free flame in a distillation flask connected with a receiver leading into a 5% hydrochloric acid

gold chloride solution catch, till the initially swelled up mass melted down. There was a copious precipitate in the gold chloride catch, which after washing melted at 222° (Trimethylamine gold chloride, m.p. 220°). The distillation flask as well as the receiver into which a few drops of a light yellow product had distilled over were exhausted with petroleum ether. A negligible reddish brown product remained undissolved. The petroleum ether solution was washed with water, and treated with ethereal HCl. The hydrochloride was treated in aqueous solution with potassium iodide. The insoluble crystalline iodide thereby obtained yielded conessine, m.p. 125–26°. The filtrate from the hydroiodide gave a very small quantity of apo-conessine (m.p. 73°) through the sulphate. The base from the mother liquors of apo-conessine sulphate gave a further quantity of conessine and a petroleum ether insoluble, cream coloured base, m.p. 225-30°, which was not sufficient for further investigation. In a second experiment 1·1 g. conessine dimethyl ammonium hydroxide was heated in a distillation flask connected with a methoxyl, N-CH_3 determination apparatus. The methyl alcohol and trimethylamine were caught up in hydriodic acid well cooled in an ice mixture and estimated. [Found : OCH_3, 1·8 ; N-CH_3, 5·92 % ; $C_{24}H_{40}N_2(CH_3OH)_2 = C_{24}H_{40}N_2 + 2CH_3OH$ requires OCH_3, 14·8 % ; $C_{24}H_{40}N_2(CH_3OH)_2 = 2H_2O + (CH_3)_3\ N + C_{23}H_{35}N$ requires N-CH_3, 10·7 %.]

The method devised above cannot claim to be quantitative in character, but it shows the direction in which the degradation proceeds.

Dry distillation of conessine dimethyl ammonium chloride.—1·2 g. conessine dimethochloride was slowly heated upto 340° at 4 mm. in a metal bath when it partly sublimed and partly distilled over. The colourless petroleum ether soluble portion of the receiver contents yielded 0·6 g. pure conessine, m.p. 124–25°, $[\alpha]_D^{37°} = +31°·2$. The petroleum ether insoluble portion was soluble in water and was evidently the sublimed original product.

When 1 g. conessine dimethochloride was heated at ordinary pressure with free flame it melted down with frothing to a reddish yellow liquid, which was soluble in petroleum ether and yielded 0·45 g. conessine, m.p. 125–26° on crystallisation from acetone.

ON THE THEORY OF LIQUIDS.

Part VI. The Rate of Reactions in Liquids.

By T. S. Wheeler.

(From the Royal Institute of Science, Bombay.)

Received June 15, 1936.

In a series of papers[1] the author has developed a modification of Edser's theory of liquids and deduced a number of equations relating various properties of liquids, one to another. In this modified theory, each molecule of a liquid, particularly near the melting-point, is regarded as vibrating within an associated spherical space of diameter σ, which it keeps clear from other molecules by virtue of its thermal motion. The vibrations take place under forces of attraction and repulsion between the molecules. In addition to this oscillatory motion, a small fraction of the molecules undergo diffusion, but near the melting-point the translatory motions are small and can be neglected. The spherical spaces are regarded as closely packed so that σ_T is related to V_T the molecular volume by the equation,

$$N\sigma_T^3 = V_T\sqrt{2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where N is the number of molecules in 1 g.-mol.

This theory leads directly to the constancy of the parachor for the surface tension of a liquid[2] has been shown to be given by the equation,

$$\gamma = \frac{\pi\mu}{4\,(m-5)\,\sigma^{m+1}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where μ and m are respectively the coefficient and index of the attractive force between the molecules. (2) combined with (1) gives

$$\gamma = \frac{\pi\mu}{4\,(m-5)} \cdot \frac{N^{\frac{m+1}{3}}}{V^{\frac{m+1}{3}} \cdot 2^{\frac{m+1}{6}}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$= P^{\frac{m+1}{3}} \Big/ V^{\frac{m+1}{3}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

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[1] See Part V, *Proc. Ind. Acad. Sci.*, 1935, **2**, 466.

[2] Part V, *loc. cit.*, p. 467.

where P is a constant. If m is put equal to 11, (4) becomes

$$\gamma = P^4/V^4 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

where P is the parachor constant.

Bradley[3] independently put forward a similar view of the structure of a liquid, and has formulated a theory of unimolecular reactions in the liquid phase, in which it is assumed that reaction of a solute molecule occurs as a result of a collision with a solvent molecule bounding its spherical space, provided that the collision involves energy exceeding the critical energy, E. In this paper Bradley's views are incorporated with the frequency equation developed by the author, in his previous papers, and are shown to lead to results which agree moderately well with the experimental observations on a number of unimolecular reactions. A theory of bimolecular reactions in solution differing from that of Bradley is also developed and applied to calculate experimental results.

Unimolecular reactions.—It has been shown[4] that the vibration frequency in its spherical space of a molecule of a liquid with a normal parachor is given by

$$\nu = \frac{8\sqrt{6}}{7\sqrt{\pi}} \frac{P^4}{\bar{V}^4} \frac{\sigma}{\sqrt{\bar{m}\bar{k}T}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (6)$$

where $\bar{k}$ is Boltzmann's constant, and $\bar{m}$ is the mass of a liquid molecule. Combining (1) and (6) and inserting the numerical values of the constants we have,

$$\nu^* = 1{\cdot}40 \times 10^{12} \frac{P^4}{V^{11/3} M^{\frac{1}{2}} T^{\frac{1}{2}}} \quad .. \quad .. \quad .. \quad .. \quad (7)$$

where M is the molecular weight of the solute. The number of collisions per second of n molecules with the surrounding molecules is accordingly $2n\nu$ which gives for the velocity constant,

$$k = 2{\cdot}8 \times 10^{12} \frac{P^4}{V^{11/3} M^{\frac{1}{2}} T^{\frac{1}{2}}} \frac{-E}{e^{RT}} \left(\frac{E}{RT}\right)^{f-1} \frac{1}{\lfloor f-1} \quad .. \quad .. \quad (8)$$

it being assumed that E is defined by $2f$ squared terms.

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[3] *J.*, 1934, 1910.

[4] Part V, *loc. cit.*, p. 471.

* It is assumed that the frequency of the solute molecule is the same for the solute in solution as for the solute in the liquid state.

From (8) we have

$$\frac{d\ ln\ k}{d\ (1/T)} = -\frac{E}{R} + \frac{11T^2\alpha}{3} + (f - \tfrac{1}{2})T \quad .. \quad .. \quad .. \quad (9)$$

where α is the thermal coefficient of cubical expansion,

$$= -\frac{E_A}{R} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

where E_A is the Arrhenius critical increment.

Hence $$E_A = E - \frac{22T^2\alpha}{3} - (2f - 1)T \quad .. \quad .. \quad .. \quad (11)$$

(8) can be transformed into

$$e^{\frac{-E}{RT}}\left(\frac{E}{RT}\right)^{f-1}\frac{1}{f-1} = \frac{3{\cdot}57 \times 10^{-13}.k.V^{11/3}M^{\frac{1}{2}}T^{\frac{1}{2}}}{P^4} \quad .. \quad .. \quad (12)$$

from which if k and f be known, E can be calculated and inserted into (11) to give E_A, which can be compared with the experimental result.

k is, of course, known from experiment; for f integral values ranging from 1 upward are tried to determine if a relatively small value (say < 5) will enable a satisfactory value of E_A to be calculated.

It will be seen from Table I that with one exception the observed values of E_A can be satisfactorily reproduced, using values of f which do not in any instance exceed 4. The agreement is as good as that obtained by Moelwyn-Hughes[5] by the application of his collision theory; for most of the reactions given in Table I he postulates values of f (his $F = f-1$) greater by 2 than are required by the present theory.

For those reactions in Table I for which f takes the value 1, it may be supposed that the two squared terms involved are to be referred to the kinetic and oscillation potential energies of the decomposing molecule; the energy of the solvent molecule is here not effective in producing decomposition.

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[5] *The Kinetics of Reactions in Solution*, Oxford, 1933, p. 164.

TABLE I.

Reaction	P‡	M	T	V†	α†$\times 10^4$	k* (obs. sec.$^{-1}$)	E_A* (obs.) cals./g.-m.	E_A (calc.) (11, 12) cals./g.-m.	f
Conversion of *d*-pinene into dipentene ..	362.5	136	457.5	186	9.4	4.99×10^{-7}	41,200	41,600	3
Decomp. of N_2O_5 in CCl_4 ..	165	108	298	67.5	10	4.09×10^{-5}	25,500	25,000	3
Decomp. of CCl_3CO_2H in $PhNH_2$ ..	252.8	163.5	298	96.7	9.6	6.70×10^{-7}	28,400	28,800	4
Decomp. of $Et_2C(COOH)_2$ in H_2O ..	365.2	160	333	157	9.5	2.00×10^{-8}	33,400	33,200	3
Decomp. of $H_2C(CO_2H)_2$ in H_2O ..	209.2	104	,,	102	,,	1.41×10^{-7}	28,800	29,800 28,000	2 1
Decomp. of *s*-trinitrobenzoic acid in H_2O ..	442.8	257	,,	183	8	3.33×10^{-6}	30,000	29,700	3
Do. in $PhNO_2$ ..	,,	,,	,,	,,	,,	4.07×10^{-9}	35,000	34,400	3
Do. in PhMe ..	,,	,,	,,	,,	,,	1.62×10^{-9}	31,600	31,400	1
Do. in PhCOMe ..	,,	,,	,,	,,	,,	$5{\cdot}79 \times 10^{-7}$	25,500	27,400	1
Decomp. of PhN_2Cl in H_2O ..	314.3	140.5	,,	114	11	3.43×10^{-3}	23,400	23,600	2
Decomp. of *p*-toluenediazonium chloride in H_2O ..	353.3	154.5	,,	125	,,	5.20×10^{-4}	27,700	27,700	4

* Bradley, *loc. cit.*; Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford, 1933, pp. 53, 54, 164.

† Where data are not available, values for compounds of a similar type or similar molecular weight have been employed; approximate values are sufficient for the purposes of calculation.

‡ Based on the figures given in Sugden, *The Parachor and Valency*, London, 1930.

The experimental values of E_A are accurate in most instances to within about $\pm$ 500 cals.

Bimolecular reactions.—We assume as before that the vibratory motions only, of the molecules need be considered. Reaction occurs when a solute molecule of type 1 collides with sufficient energy, with one of type 2 which bounds its spherical space. If n_1, n_2 and n_s denote respectively, the number of solute molecules of type 1 and 2, and of molecules of the solvent in 1 c.c., then the number of collisions which the n_1 molecules of type 1 make with the boundaries of their spherical spaces is $2n_1\nu_1$ per sec. The number of these collisions which involve molecules of type 2 is

$$Z_{12} = 2n_1\nu_1 \frac{n_2}{n_s + n_1 + n_2} = \frac{2n_1n_2\nu_1}{n_s} \quad .. \quad .. \quad .. \quad (13)$$

since n_s is large compared with n_1 and n_2.

Similarly, the number of collisions per sec. of n_2 molecules of type 2 with molecules of type 1 is given by

$$Z_{21} = \frac{2n_1n_2\nu_2}{n_s} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (14)$$

Z_{12} and Z_{21} should be identical, but are not so, because in each calculation the frequency of one type of molecule only has been considered. We may, however, as an approximation use the mean of the frequencies and put

$$Z_{12} = Z_{21} = \frac{n_1n_2}{n_s}(\nu_1 + \nu_2) \quad .. \quad .. \quad .. \quad .. \quad (15)$$

The number of fruitful collisions per sec. with critical energies greater than E will then be

$$\frac{n_1n_2}{n_s}(\nu_1 + \nu_2)\, e^{\frac{-E}{RT}} \left(\frac{E}{RT}\right)^{f-1} \frac{1}{\underline{f-1}}.$$

Hence the rate of chemical change becomes

$$\frac{dn}{dt} = \frac{n_1n_2}{n_s}(\nu_1 + \nu_2) e^{\frac{-E}{RT}} \left(\frac{E}{RT}\right)^{f-1} \frac{1}{\underline{f-1}} \quad .. \quad .. \quad .. \quad (16)$$

The bimolecular velocity constant expressed in litres per g.-mol. per sec. is given by

$$k = \frac{1}{n_1n_2}\frac{dn}{dt}\frac{N}{1000} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (17)$$

so that we have

$$k = \frac{N}{1000}\frac{\nu_1 + \nu_2}{n_s} e^{\frac{-E}{RT}} \left(\frac{E}{RT}\right)^{f-1} \frac{1}{\underline{f-1}} \quad .. \quad .. \quad .. \quad (18)$$

Inserting the values of ν_1 and ν_2 [see (7)] and putting $n_s = \frac{N}{V_s}$

we have

$$k = \frac{(1\cdot40\times10^{9})\ V_s}{T^{\frac{1}{2}}}\left(\frac{P_1^{4}}{V_1^{11/3}\,M_1^{\frac{1}{2}}} + \frac{P_2^{4}}{V_2^{11/3}\,M_2^{\frac{1}{2}}}\right)e^{\frac{-E}{RT}}\left(\frac{E}{RT}\right)^{f-1}\frac{1}{\lfloor f-1}\quad (19)$$

and

$$e^{\frac{-E}{RT}}\left(\frac{E}{RT}\right)^{f-1}\frac{1}{\lfloor f-1} = \frac{(7\cdot14\times10^{-10})T^{\frac{1}{2}}k}{V_s}\left[\frac{P_1^{4}}{V_1^{11/3}\,M_1^{\frac{1}{2}}} + \frac{P_2^{4}}{V_2^{11/3}\,M_2^{\frac{1}{2}}}\right]^{-1} \quad (20)$$

To differentiate k we write (19) in the following approximate form,

$$k = (1\cdot40\times10^{9})\ V_s\ \frac{2P^{4}}{V^{11/3}\,M^{\frac{1}{2}}T^{\frac{1}{2}}}\,e^{\frac{-E}{RT}}\left(\frac{E}{RT}\right)^{f-1}\frac{1}{\lfloor f-1} \quad .. \quad (21)$$

where P^4, $V^{11/3}$ and $M^{\frac{1}{2}}$ are the averages of respectively, $P_1^4\,P_2^4$, $V_1^{11/3}V_2^{11/3}$, and $M_1^{\frac{1}{2}}\,M_2^{\frac{1}{2}}$. Differentiating (21) we obtain,

$$\frac{d\ ln\ k}{d(1/T)} = -\frac{E_A}{R} = -\frac{E}{R} - T^2\alpha_s + \frac{11}{3}\,T^2\alpha + \frac{T}{2}(2f-1) \quad .. \quad (22)$$

$$= -\frac{E}{R} + \frac{8}{3}\,T^2\alpha_s + \frac{T}{2}\,(2f-1)\ .. \quad .. \quad (23)$$

since α may be put equal to α_s without serious error. We now proceed as before to calculate E from(20) and thence E_A from (23) using small integral values of f.

Bradley[6] has pointed out that suitable examples of bimolecular reactions between unionised molecules are rare, but that no serious difficulty is introduced, if one of the reactants is an unionised molecule, and the ions considered are not strongly solvated. It will be seen from Table II that for a variety of such reactions, the experimental value of E_A can be reproduced with values of f equal to 1 or 2 indicating that the critical energy of collision for bimolecular reactions involves few internal degrees of freedom.

It would appear, therefore, that the theory of the structure of liquids, which has been developed by the author, is capable of affording a satisfactory picture of the mechanism of simple unimolecular and bimolecular reactions in solution.

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[6] *Loc. cit.*, p. 1916.

TABLE II.

Reactant 1	Reactant 2	Solvent	P_1‡	V_1†	P_2‡	V_2†	V_s	a_s	T	k* (litres per g.-m.-sec.)	E_A* (obs.) (cals./g.-m.)	E_A (calc.) (20,23)	f
1 : 2 : 4 Dinitrochlorobenzene ..	EtONa	EtOH	356.1	150	195.1	70	58	0.0011	291	6.0×10^{-2}	16,800	16,000 17,400	1 2
,,	MeONa	MeOH	,,	,,	156.1	56	40	0.0012	,,	1.78×10^{-2}	17,400	16,500 17,900	1 2
MeI ..	EtONa	EtOH	147.1	62.5	195.1	70	58	0.0011	,,	4.96×10^{-4}	19,500	18,800 20,300	1 2
EtI	EtONa	,,	186.1	81	,,	,,	,,	,,	,,	5.92×10^{-5}	20,600	20,000 21,600	1 2
EtBr	Et_2S	$PhCH_2OH$	163.1	83	238.4	123	108	0.0007	353	2.44×10^{-5}	24,500	24,600	1
$PhCH_2I$	EtONa	EtOH	320	125	195.1	70	58	0.0011	291	2.38×10^{-5}	19,900	20,600	1
PhONa	PrI	,,	290	100	225.1	97	,,	,,	,,	6.29×10^{-6}	22,400	21,300 23,000	1 2

* Bradley, *loc. cit.*; Moelwyn-Hughes, *op. cit.*, pp. 77, 79.

† ‡ See ft.-notes 2 and 3, Table I.

The errors in the experimental values of E_A range up to ± 1000 cals.

ON THE THEORY OF LIQUIDS.

Part VII. Diffusion and Vapour Pressure Phenomena.

By T. S. Wheeler.

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In a series of papers,[1] the author has developed a modification of Edser's theory of liquids, and deduced a series of equations relating various properties of liquids one to another. In this modified theory, each molecule of liquid particularly near the melting-point, is regarded as vibrating within an associated spherical space of diameter σ, which it keeps clear from other molecules by virtue of its thermal motion. The vibrations take place under the forces of attraction and repulsion between the molecules. In addition to this oscillatory motion, a small fraction of the molecules undergo diffusion; it is with this phenomenon that we are now concerned.

Bradley[2] independently put forward a similar view of the structure of a liquid. On his theory, diffusion occurs when a vibrating solute molecule has sufficient kinetic energy (W per g.-mol.) to break through the boundary of its associated spherical space. He deduces for the diffusion coefficient D the formula,

$$D = \frac{d^2}{6\tau} e^{\frac{-W}{RT}} \quad .. \quad .. \quad .. \quad (1)$$

where τ is the time of half vibration of a molecule in its associated spherical space, and d is taken to be the sum of the radii of the molecules of the solvent and the solute.

We can rewrite this equation in the form,

$$D = \frac{\sigma^2 \nu}{3} e^{\frac{-W}{RT}} \quad .. \quad .. \quad .. \quad (2)$$

where ν is the vibration frequency of the molecule, and σ the molecular diameter of the solute is put for d; the magnitude of the change involved in the substitution is not great.

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[1] See Part V, *Proc. Ind. Acad. Sci.*, 1935, **2**, 466; Part VI, preceding paper.

[2] *J.*, 1934, 1910.

It has been shown[3] that the vibration frequency of a molecule with a normal parachor P is given by

$$\nu = \frac{8\sqrt{6}}{7\sqrt{\pi}} \frac{P^4}{V^4} \frac{\sigma}{\sqrt{\bar{m}kT}} \quad .. \quad .. \quad .. \quad (3)$$

where k is Boltzmann's constant, $\bar{m}$ is the mass of the molecule, and V is the molecular volume of the solute in the liquid state. Further, as the molecular spaces in the liquid state are regarded as closely packed, σ is related to V by the equation

$$N\sigma^3 = V\sqrt{2} \quad .. \quad .. \quad .. \quad .. \quad (4)$$

where N is the number of molecules in 1 g.-mol. Combining (2), (3) and (4) we have

$$D = 8{\cdot}17 \times 10^{-5} \frac{P^4 e^{\frac{-W}{RT}}}{V^3 M^{\frac{1}{2}} T^{\frac{1}{2}}} \quad .. \quad .. \quad (5)$$

where M is the molecular weight of the substance diffusing.

In applying his equation, Bradley used a different expression for the frequency, and considered the critical energy for passage through the barrier as being defined by two squared terms only. This is probably true as regards the kinetic energy which molecule must possess in order to do the work necessary for its passage through the barrier. But there will normally be a latent heat associated with this work and greater than it, just as the internal heat of vaporisation is associated with a lesser work of vaporisation. This additional energy may be referred to the internal degrees of freedom of the molecule, which are increasingly energised as the kinetic energy of the molecule increases. We accordingly modify (5) by assuming that the total critical energy E is defined by $2f$ squared terms and write,

$$D = 8{\cdot}17 \times 10^{-5} \frac{P^4}{V^3 M^{\frac{1}{2}} T^{\frac{1}{2}}} \left(\frac{E}{RT}\right)^{f-1} \frac{e^{RT}}{\underline{|f-1}} \quad .. \quad .. \quad (6)$$

that is,

$$e^{\frac{-E}{RT}} \left(\frac{E}{RT}\right)^{f-1} \frac{1}{\underline{|f-1}} = \frac{1{\cdot}23 \times 10^4 \, DV^3 T^{\frac{1}{2}} M^{\frac{1}{2}}}{P^4} \quad .. \quad (7)$$

We can put (6) in the form,

$$ln\, D = ln\, K_1 - 3\, ln\, V - \frac{E}{RT} + \frac{2f-1}{2} ln \frac{1}{T} \quad .. \quad (8)$$

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[3] Part V, *loc. cit.*, p. 471.

where K_1 is a constant. This on differentiation gives

$$\frac{d\ ln\ D}{d\left(\frac{1}{T}\right)} = \frac{-E}{R} + 3T^2\alpha + \frac{T(2f-1)}{2} \quad .. \quad .. \quad (9)$$

$\left(\alpha = \frac{1}{V}\frac{dV}{dT}, \text{ is the coefficient of thermal expansion.}\right)$

$$= -\frac{E_1^*}{R} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

so that

$$\frac{E_1}{RT} = \frac{E}{RT} - 3T\alpha - \frac{2f-1}{2} \quad .. \quad .. \quad .. \quad (11)$$

To test (7) we assume f to be an integer, and calculate E from it, and thence E_1 from E by means of (11). If (7) is valid, it should be possible to duplicate the observed values of E_1 (obtained by plotting in D against 1/T) by using small integral values of f. Experimental data are limited, but as Table I shows, satisfactory agreement between observed and calculated values of E_1, can be obtained in three instances for which experimental results are available.

TABLE I.

Solute	Solvent	T	V solute	P solute	α solute	D* (obs.)	E_1* (obs.)	E_1 (calc.) (7); (11)	f
							cal./g.—m.		
PhOH	MeOH	294	89	227·1	$8{\cdot}3\times10^{-4}$	$1{\cdot}62\times10^{-5}$	3200	3300	4
,,	C_6H_6	,,	,,	,,	,,	$1{\cdot}69\times10^{-5}$	3100	3200	,,
$C_2H_2Br_4$	$C_2H_2Cl_4$	,,	117	315·8	$6{\cdot}8\times10^{-4}$	$5{\cdot}62\times10^{-6}$	3400	3300	2

* Bradley, *loc. cit.*, pp. 1914, 1915.

Vapour pressure.—In Part III of this series[4] a formula relating the vapour pressure to the internal latent heat of vaporisation was deduced. This formula was based on the idea that a molecule vibrating in the surface layer of a liquid vaporised when it acquired a kinetic energy normal to the surface greater than the work required to remove it to an infinite distance.

* Bradley (*loc. cit.*, p. 1914) has shown that a plot of *ln*D against 1/T gives a straight line.

[4] *Proc. Ind. Acad. Sci.*, 1935, **1**, 803.

The values for the work of vaporisation thus calculated were multiplied by

$$\left[1 + \frac{T(m - 4)\alpha}{3}\right]^5$$

to give the internal heat of vaporisation which was compared with the observed value. The calculated results were higher than the experimental results by up to 8%. The following alternative method of treatment is now put forward.

The number of molecules in a surface plane of unit area is given by

$$n' = \frac{2}{\sqrt{3}\,\sigma^2} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (12)$$

since the spherical spaces associated with the molecules are closely packed. As a first approximation, it may be assumed that one-third of the n' molecules are vibrating normally to the surface.

In Part III,[6] it has been shown that the frequency of a surface molecule is approximately the same as that of one in the interior of the liquid, which frequency is given by (3) above. Hence if E_2 is the total critical energy for escape, the number of vibrations per second normal to the surface associated with an energy defined by $2f$ squared terms and greater than E_2 is given by

$$N_e = \frac{n'}{3}\,\nu\left(\frac{E_2}{RT}\right)^{f-1}\frac{e^{\frac{-E_2}{RT}}}{\lfloor f-1}} \quad .. \quad .. \quad .. \quad (13)$$

where N_e is thus the number of molecules leaving the surface per second.

The number of molecules from the vapour phase which strike unit area of the surface per second is given by

$$N_g = \frac{N}{V_g}\sqrt{\frac{kT}{2m\pi}} \quad .. \quad .. \quad .. \quad .. \quad (14)$$

where V_g is the molecular volume of the vapour.

If the dilute vapour is considered to be a perfect gas we can write,

$$p = \frac{NkT}{V_g} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (15)$$

where p is the vapour pressure expressed in dynes per sq. cm.

Hence from (14) and (15),

$$N_g = \frac{p}{\sqrt{2mkT\pi}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (16)$$

At equilibrium we can put,

$$N_e = N_g\dagger \quad .. \quad .. \quad .. \quad .. \quad .. \quad (17)$$

---

[5] See equation (20), Part I, *Ind. J. Phys.*, 1934, **8**, 527.

[6] *Loc. cit.*, p. 804.

† It is assumed that all molecules which strike the liquid surface from the vapour phase are condensed. This is probably approximately true with the liquids considered.

so that from (13), (16) and (17),

$$\frac{n'\nu}{3}\left(\frac{E_2}{RT}\right)^{f-1}\frac{e^{\frac{-E_2}{RT}}}{\lfloor f-1}=\frac{p}{\sqrt{2\pi mkT\pi}} \quad .. \quad .. \quad .. \quad (18)$$

Inserting (3), (4) and (12), transposing, and substituting the numerical values of the constants, we have

$$e^{\frac{-E_2}{RT}}\left(\frac{E_2}{RT}\right)^{f-1}\frac{1}{\lfloor f-1}=\frac{1{\cdot}15\times10^{-5}\,p'\,V^{\frac{13}{3}}}{P^4} \quad .. \quad (19)$$

where p' is expressed in mm. per sq. cm.

We can write (19) in the form,

$$ln\,p'=ln\,K_2-\tfrac{13}{3}\,ln\,V-\frac{E_2}{RT}+(f-1)\,ln\frac{1}{T} \quad .. \quad (20)$$

(K_2 is a constant), which gives,

$$\frac{d\,ln\,p'}{d\left(\frac{1}{T}\right)}=\frac{-E_2}{R}+\tfrac{13}{3}\,T^2a+T(f-1) \quad .. \quad .. \quad (21)$$

$$=-\frac{L_t}{R} \quad .. \quad .. \quad .. \quad .. \quad (22)$$

where L_t is the observed heat of vaporisation at temperature T.

Hence

$$\frac{L_t}{RT}=\frac{E_2}{RT}-\frac{13Ta}{3}-(f-1) \quad .. \quad .. \quad .. \quad (23)$$

To test (19) we calculate E_2 from it using integral values of f, and thence L_t by means of (23), and see if the observed values of L_t can be duplicated. As Table II shows, concordance between the observed and calculated values of L_t is obtained with values of f from 7 to 9.

TABLE II.

Substance	T	p' mm.	P	V	L (obs.)	L (calc.) (19); (23)	f
					cals./g.—mol.		
C_6H_6	279	37	207·1	87·3	8300	8200	8
$CHCl_3$	253	20	184·8	76·3	8100	8100	8
CCl_4	,,	10	222·0	92·0	8200	8200	7
C_6H_{14} (n)	,,	14	268·2	124	8200	8200	9

The author's thanks are due to Mr. R. S. Bradley for his valuable advice.

ORGANO-METALLOID COMPOUNDS. PART I.

By Sudhirchandra Nivogy.

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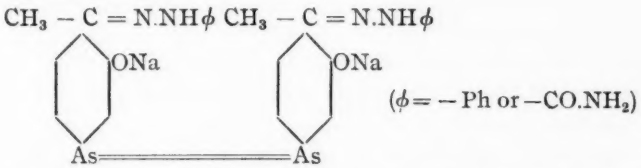
Until recently it was assumed that for the preparation of an active trypanocide (among arsenicals) the structure of the compound must correspond to the salvarsan type, *i.e.*, the compound must be derived from 3-nitro-4-hydroxyphenylarsenic acid. In fact, any deviation from this type was attended with diminished activity or increased toxicity. It has been recently demonstrated by Albert[1] that compounds having no similarity to salvarsan in structure, may also possess trypanocidal activity not inferior to salvarsan or its allied products. The substance in question is known as " Albert 102 " having the following constitution :—



The substance thus appears to be a semicarbazone or phenylhydrazone of the corresponding ketone. That either of these groupings may have any effect in the appearance of trypanocidal properties in an arsenical, is noticed for the first time in " Albert 102 ". The function of the hydroxyl group might be to render the product capable of forming soluble salts, since it has been found that acetophenone-4-arsenic acid has a therapeutic activity between 4 and 6.

As in the case of the trivalent arseno-compounds, the presence of amino and hydroxyl groups in particular positions were considered essential, so also in the case of the stibinic acids employed for the treatment of Indian Kala-azar, it is still maintained that therapeutically active compounds must be derived from 4-aminophenylstibinic acid. But considering the case of " Albert 102 ", the preparation of the corresponding stibinic acid was undertaken to find, whether it exhibits any activity or not ; since however, the trivalent stibino-compounds are very unstable, the true antimony analogue of

[1] *Klin. Woch.*, 1924, **48**, 2184.

" Albert 102 ", could not be prepared, the corresponding stibinic acid being the final product of this investigation.

For the preparation of semicarbazone of acetophenone 2-hydroxy-4-stibinic acid, an attempt was first made to prepare 2-hydroxy-4-aminophenyl methyl ketone by the nitration of 4-acetylaminoacetophenone in sulphuric acid solution with nitric acid (d 1·40) but unfortunately this scheme could not be worked upon, as the isomeric 2-nitro- and 3-nitro-4-acetylaminoacetophenone, which were produced simultaneously, could not be separated.[2] The method that was finally adopted for the preparation of the required compound consisted in the preparation of 4-acetylaminoacetophenone[3] with some modification. Kunchell[3] (*loc. cit.*) employed acetylbromide, acetanilide and aluminium chloride. We substituted acetyl chloride for the bromide and succeeded in getting an excellent yield by adding the acid chloride to a mixture of acetanilide and aluminium chloride in dry carbon disulphide. When, however, aluminium chloride was added gradually to a mixture of the acid chloride and acetanilide in carbon disulphide, the reaction did not take place and unchanged acetanilide was obtained at the end of the operation. 4-Acetylaminoacetophenone was then hydrolysed and the free amine diazotised in hydrochloric acid solution and treated with a solution of antimony trichloride in hydrochloric acid. It is generally found that an additive compound of the diazonium chloride and antimony trichloride separates at once but in this case, the additive compound was found to be rather soluble in hydrochloric acid and the concentration of the acid was carefully regulated so that no antimony oxychloride separated. After the usual alkaline decomposition of this additive compound at a low temperature, the free stibinic acid was isolated by acidifying the reaction liquid with dilute sulphuric acid (the stibinic acid is soluble in acetic acid). Acetophenone-4-stibinic acid (sodium salt) was dissolved in formic acid solution or in a mixture of acetic acid and formic acid[4] and slowly added to concentrated sulphuric acid at 0—0·5° and then nitrated as usual. The nitrated product was collected as usual by diluting the acid solution with crushed ice. The nitrostibinic acid was found to be soluble in alcohol and the crude product was purified by dissolving in alcohol and precipitating the stibinic acid with water. The ketone was then converted into its semicarbazone and the nitro-group reduced, with aluminium mercury couple. The free ketone was then regenerated by warming with dilute hydrochloric

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[2] Gibson and Levin, *J. C. S.*, 1931, 2388.

[3] Kunchell, *Ber.*, 1900, **33**, 2642.

[4] *D. R .P.*, 259,875; 287,709.

acid and the amino-group replaced by hydroxyl through diazo reaction. The keto group was again converted into its semicarbazone.

The constitution of the nitration product of acetophenone-4-stibinic acid, described before, is a matter of uncertainty. The orienting influence of both SbO_3H_2 and $CO.CH_3$ is *meta*. But in our experiments, the main product isolated is acetophenone-2-nitro-4-stibinic acid. The constitution of this was established by the following reactions :—Nitroacetophenone stibinic acid was treated with dilute sulphuric acid and potassium iodide when the antimony complex was removed and replaced by iodine, the product thus isolated being 2-nitro-4-iodoacetophenone. On oxidation with alkaline permanganate, $-CO.CH_3$ was converted into -COOH group giving 2-nitro-4-iodobenzoic acid. By distillation with soda lime, the carboxyl group was removed giving 3-nitroiodobenzene identical with an authentic sample in every respect. Thus it is clear that in this case the nitration product isolated by us is 2-nitro-acetophenone 4-stibinic acid.

The physiological action of the final product—semicarbazone of 2-hydroxy acetophenone-4-stibinic acid—was not satisfactory. The M. L. D. for white mice lies between 150 and 200 mg. per kg., but it was found to have only a slight action in cases of Kala-azar and that only in its early stages.

Experimental.

4-*Acetylaminoacetophenone.*—This was prepared by a modification of the method described by Kunchell.[5] To a mixture of acetanilide (10 g.) and anhydrous aluminium chloride (30 g.) in carbon disulphide (25 c.c.) under reflux, acetyl chloride (15 c.c.) was added gradually with vigorous agitation during 30 minutes. The reaction was then completed by heating on a water-bath for 1 hour and excess of carbon disulphide was distilled off. The dark red oily reaction product was then well cooled in ice and then treated with ice cold dilute hydrochloric acid. A pasty light brown solid was thus obtained which was filtered off and recrystallised from water (charcoal) as light brown crystals, m. p. 166–67° ; yield 7·5 g.

Hydrolysis.—The hydrolysis of the acetyl group was carried out according to the method of Kunchell (*loc. cit.*). The crude product was crystallised from water, in glistening yellow plates, m. p. 104–5°.

Acetophenone-4-stibinic acid.—4-Aminoacetophenone (10 g.) was dissolved in water (30 c.c.) and hydrochloric acid (7·5 c.c.). The solution was cooled to 0° and diazotised with the addition of sodium nitrite (5 g.) in water (20 c.c.). A solution of antimony trichloride (7 g.) in hydrochloric acid (25 c.c.) was then

[5] *Ber.*, 1900, **33**, 2642.

gradually added to the diazzo solution and the precipitated yellowish white solid was filtered off, washed first with hydrochloric acid (d. 1·12) and then with water. The moist mass was then suspended in water, cooled to 10° and a solution of caustic soda added, under vigorous stirring, till faintly alkaline. After the evolution of nitrogen has slackened off (1 hour), the liquid was nearly neutralised with dilute sulphuric acid and saturated with carbon dioxide for 15 minutes. The dark coloured residue was filtered and the filtrate acidified with dilute sulphuric acid when the free stibinic acid separated as a light brown gelatinous mass. The precipitate was allowed to stand overnight in a refrigerator and filtered off. It was then suspended in water and dissolved by the gradual addition of dilute caustic soda till faintly alkaline. The alkaline solution was then evaporated to dryness *in vacuo* over sulphuric acid and the brown residue repeatedly extracted with methyl alcohol, filtered and the filtrate treated with excess of ether when the sodium salt separated as a light brown mass. This was again filtered off, washed with ether and dried *in vacuo* over liquid paraffin (yield 3 g.). [Found : C, 30·7 ; H, 3·12 ; Sb, 39·2%. $C_8H_8O_4SbNa$ requires C, 30·9 ; H, 2·57 ; Sb, 38·58%.]

Properties.—The sodium salt was a light red amorphous powder, decomposing between 220 and 40° without melting. It is very soluble in alcohol and a concentrated solution in water gave no precipitate when treated with large excess of alcohol. When an aqueous solution was first acidified with dilute sulphuric acid, the free stibinic acid separated which however dissolved in excess of dilute acetic acid. On the addition of barium or calcium chloride insoluble barium or calcium salt of the stibinic acid separated as an amorphous mass.

2-*Nitro-acetophenone*-4-*stibinic acid.*—Sodium salt of acetophenone-4-stibinic acid (5·5 g.) was dissolved in anhydrous formic acid (40 c.c.) and added very slowly to concentrated sulphuric acid (25 c.c.) cooled to 0°, with mechanical stirring. A mixture of nitric acid (1·5 c.c., d. 1·40) and sulphuric acid (10 c.c., d. 1·84) was then slowly added to the cooled sulphuric-formic acid solution of the stibinic acid at 0°–5° with gentle stirring. The stirring was continued for 60 minutes after the addition of the whole of the nitrating acid. The thick brown liquid was then poured into crushed ice (100 g.) when a light red gelatinous mass separated. The mass was separated by centrifuging the liquid and was washed free from acid with water. Contrary to our expectations, this stibinic acid was found to be rather soluble in alcohol and its purification was effected by dissolving the solid in rectified spirit and adding an excess of water when the free stibinic acid was precipitated (twice). Finally it was dried *in vacuo* over fused calcium chloride

(yield 3·5 g.): [Found: N, 3·80; Sb, 35·7; C, 26·53; H, 2·85%. $C_8H_8O_6NSb$ requires N, 4·1; Sb, 35·9; C, 26·98; H, 2·41%.]

Properties.—The nitro-stibinic acid was found to be a light brown solid easily soluble in alkali or alkali carbonate and precipitated by the addition of mineral acids or acetic acid. On being heated with concentrated hydrochloric acid and then diluting and treating with sulphurated hydrogen, an orange precipitate of antimony sulphide was obtained. As stated before it was soluble in alcohol and insoluble in water. Insoluble calcium or barium salts were thrown down when a solution of the sodium salt was treated with calcium or barium chloride.

Semicarbazone of 2-nitro-acetophenone-4-stibinic acid.—The semicarbazone was prepared from the ketone by dissolving the nitroketonic stibinic acid in dilute caustic soda (avoiding excess) and warming on a water-bath for several hours with semicarbazide. A white precipitiate of the antimony oxide separated during the heating and was removed by filtration. The free stibinic acid was then precipitated by adding dilute acetic acid, filtered and washed repeatedly with cold dilute hydrochloric acid to remove excess of semicarbazide. The sodium salt was then prepared as usual and was precipitated by the addition of alcohol (twice). Finally it was filtered off, washed and dried as usual *in vacuo*. [Found: N, 12·8; Sb, 28·70; C, 26·58; H, 3·2%. $C_9H_{10}O_6N_4SbNa$ requires N, 13·5; Sb, 29·05; C, 26·11; H, 2·52%.]

Properties.—It is a light pink amorphous powder, freely soluble in water forming a red solution. On acidifying with dilute hydrochloric acid and adding sodium nitrite, copious evolution of nitrogen was noticed.

Semicarbazone of acetophenone 2-amino-4-stibinic acid.—The corresponding nitro compound (2 g.) was dissolved in water (50 c.c.) and gradually treated with aluminium mercury couple (4 g.) in the course of 4 hours. After standing overnight, the precipitated aluminium hydroxide was filtered off and the precipitate twice extracted with dilute sodium carbonate and the filtrate and the extracts saturated with carbon dioxide. After filtration from the separated solid, the clear liquid was acidified with dilute acetic acid when a gelatinous precipate separated. On examination, this was found to be the desired product and was converted into sodium salt by treatment with the required quantity of sodium carbonate and the aqueous solution subsequently precipitated by alcohol when the sodium salt separated as a light pink amorphous mass (yield 1 g.). [Found: Sb, 31·67; C, 27·9; H, 3·6%. $C_9H_{12}O_4N_4SbNa$ requires Sb, 31·33; C, 28·2; H, 3·1%.]

Properties.—It is a faint pink powder, easily soluble in water to a red solution. When treated with dilute acetic acid, it gave a precipitate which

dissolved in dilute hydrochloric acid. It gives diazo reaction with evolution of nitrogen.

2-Aminoacetophenone 4-stibinic acid.—This was prepared from the above compound by splitting off the semicarbazide by heating with 25% hydrochloric acid. It was found however that a considerable part of the stibinic acid itself was decomposed during this heating, as the stibinic acids are unstable in presence of strong mineral acid. After filtering off the insoluble bye-products the liquid was cooled in a freezing mixture and treated with freshly prepared ice-cold fuming hydrochloric acid (d. 1·20) when a white precipitate separated. This was found to be hydrochloride of the amino body and was filtered off in the cold. It was then dissolved in a small quantity of ice cold water and saturated with sodium acetate when a precipitate separated which was found to be the required stibinic acid. Sodium chloride and excess of sodium acetate was removed by repeated washing with distilled water and the free stibinic acid was converted into sodium salt as described before. [Found: Sb, 35·2; C, 28·9; H, 3·25; N, 3·71%. $C_8H_9O_4NSbNa$ requires Sb, 35·7; C, 29·4; H, 2·72; N, 4·3%.]

Properties.—The sodium salt found to be soluble in water and in dilute mineral acids. It gave diazo reaction without evolution of nitrogen.

Semicarbazone of 2-hydroxy acetophenone 4-stibinic acid.—The regenerated aminoketone stibinic acid was dissolved in dilute hydrochloric acid, cooled to 0° and diazotised with the necessary quantity of sodium nitrite, the liquid was then allowed to stand at ordinary temperature till evolution of nitrogen had ceased (3 hours). A precipitate was found to have separated during this time, which was removed by filtration, washed and dissolved in dilute sodium carbonate. Semicarbazide (2 g.) was dissolved in water (10 c.c.) and neutralised with dilute alkali. The two solutions were mixed and heated on a water-bath at 60–80° for 2 hours and allowed to stand overnight. The liquid was then filtered, acidified with dilute hydrochloric acid and the resulting precipitate washed first with dilute hydrochloric acid and then with water. It was then converted into sodium salt as usual. [Found: N, 10·2; Sb, 30·9; C, 27·85; H, 3·2%. $C_9H_{11}O_5N_3SbNa$ requires N, 10·9; Sb, 31·2; C, 28·13; H, 2·98%.]

The author is greatly indebted to Prof. Dr. H. K. Sen, for the interest taken in this work and also for placing all the resources of his laboratory at his disposal.

ORGANO-METALLOID COMPOUNDS. PART II.

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In a previous communication,[1] an attempt was made for preparing hydroxymethyl-phenyl-stibinic acids with a view to ascertain the physiological action, if any, of the hydroxymethyl group, in the treatment of Indian Kala-azar. From the published literature, it has been established that an antimonial, in order to be effective for the treatment of the disease caused by Leishmann-Donovann bodies, must confirm to the structure of 4-aminophenylstibinic acid. Relying on this observation, an attempt was made to prepare 5-amino 2-acetylaminobenzyl alcohol which by the application of well-known Bart-Schmidt reaction would give 2-acetylaminobenzylalcohol-5-stibinic acid. At the same time it was also considered to be of interest to investigate whether a stibinic acid with a CH_2OH group in – *o* – or *m*-position exhibits any marked physiological activity.

5-Nitro-2-acetylaminobenzyl alcohol was prepared by the method of Cohn and Springer,[2] from the acetyl derivative of 2-aminobenzaldehyde by nitration in sulphuric acid solution and Cannizaro's reaction, followed by subsequent acetylation. On reduction with iron and acetic acid, the nitro group was reduced to the amino body from which the stibinic acid was prepared as usual by diazo reaction. 3-Acetylaminobenzylalcohol-4-stibinic acid was prepared by the following series of reactions: 4-Nitro benzaldehyde, by Cannizaro's reaction, gave 4-nitrobenzyl alcohol which was smoothly reduced to the amino body in moist ether solution with Al-Hg couple. The method of reduction with zinc dust and calcium chloride[3] was found to be a tedious one to work with. By heating with acetic anhydride and sodium acetate,[4] a diacetyl derivative m.p. 102° was obtained. On nitration with fuming nitric acid at 0–10°, 3-nitro-4-acetylaminobenzyl acetate was isolated in good yield, m.p. 82–83°. Deacetylation was effected as usual by heating with alcoholic sodium hydroxide. By diazotising the amino body in alcoholic

[1] *J. Indian Chem. Soc.*, 1931, **8**, 59.
[2] *Monatsh.*, 1903, **24**, 96.
[3] Fischer, *Ber.*, 1895, **28**, 880.
[4] Fourneau and Lestrange, *Bull. Soc. Chim.*, 1933, **5**, 330.

hydrochloric solution and treating with antimony chloride, an additive compound of the diazonium chloride and antimony trichloride was obtained which was converted into the corresponding stibinic acid in pyridine solution (*cf.* Eng. Pat. 313,58 of 1928). After the reaction was over, the stibinic acid was isolated by dilution with water. The nitro-compound was reduced with ferrous hydroxide at 0–5° to 2-aminobenzylalcohol-4-stibinic acid, the acetyl derivative of which was prepared as usual.

The physiological action of the compounds described in the experimental part is now being investigated.

Experimental.

Benzylalcohol-4-stibinic acid.—4-Aminobenzyl alcohol (12·3 g.) was dissolved in hydrochloric acid (15 c.c., d. 1·12) and diazotised with a solution of sodium nitrite (6·9 g.) at 0°. To this solution was added a solution of antimony trichloride prepared by dissolving antimony trioxide (14 g.) in hydrochloric acid (30 c.c., d. 1·18). After being stirred for a minute or two, a white crystalline solid separated. This was filtered off, washed free from antimony trichloride with dilute hydrochloric acid (d. 1·12) and then with water. The solid was then suspended in water, cooled to a temperature of 5–10° and a dilute solution of caustic soda gradually added to the suspension, with vigorous mechanical stirring, till distinctly alkaline in reaction. Vigorous evolution of nitrogen occurred and the stirring gear was kept in motion till the evolution of nitrogen had slackened. The alkaline liquid was then nearly neutralised with dilute sulphuric acid and saturated with carbon dioxide. The whole was then filtered and the filtrate acidified with dilute acetic acid when the stibinic acid separated as a gelatanious precipitate. The stibinic acid was removed by centrifuging the liquid and freed from soluble inorganic impurities by dialysis. The insoluble impurities were then removed by dissolving the dialysed stibinic acid in dilute sodium carbonate solution and filtering off the insoluble impurities, if any. The slightly alkaline solution was then filtered and the pure stibinic acid precipitated by acidification with dilute acetic acid. The stibinic acid was then removed by filtration and washed repeatedly with water and alcohol till free from sodium acetate. It was then dried over fused calcium chloride *in vacuo*. [Found : C, 30·17 ; H, 3·42 ; Sb, 43·21%. $C_7H_9O_4Sb$ requires C, 30·32 ; H, 3·25 ; Sb, 43·32 %.]

The sodium salt was prepared by dissolving the acid in the requisite quantity of dilute caustic soda, concentrating the solution *in vacuo* and precipitating the solution with a mixture of alcohol and ether. Light pink amorphous solid, decomposing on heating to 220° without melting. Very soluble in water. [Found : Na, 7·75 % ; $C_7H_8O_4SbNa$ requires Na, 7·68 %.]

Insoluble calcium and barium salts may be prepared by adding calcium or barium chloride to a solution of the sodium salt.

Benzylalcohol-3-stibinic acid.—This compound was prepared in the manner as described in the previous paragraph, from 3-aminobenzyl alcohol.

The sodium salt was prepared by dissolving the stibinic acid in dilute caustic soda and evaporating it to dryness *in vacuo*. The dry residue was then extracted with methyl alcohol or acetone, filtered and the filtrate treated with excess of ether when the sodium salt separated as a light pink amorphous mass. Filtered and dried *in vacuo* over liquid paraffin. [Found : C, 28·24 ; H, 2·82 ; Sb, 43·32 ; Na, 7·61 %; $C_7H_8O_4SbNa$ requires C, 28·09 ; H, 2·67 ; Sb, 43·47 ; Na, 7·68 %.]

Benzylalcohol-2-stibinic acid.—[Found : C, 30·31; H, 3·67; Sb, 43·33 %. $C_7H_9O_4Sb$ requires C, 30·32 ; H, 3·25 ; Sb, 43·32 %.]

5-Amino-2-acetylaminobenzyl alcohol.—Reduced iron dust (10 g.), acetic acid (4 c.c.) and water (50 c.c.) were placed in a round bottomed flask. 5-Nitro-2-acetylaminobenzylalcohol (10 g.) was gradually added to the mixture with vigorous stirring. The mixture warmed up and the temperature rose up to 50°. Further quantities of the nitro-compound was gradually added to this warm mixture during 60 minutes. After about two hours, the flask was warmed on a water-bath and a dilute solution of sodium carbonate (2 g.) in water (20 c.c.) was added. The sludge was filtered off with suction and the residue repeatedly extracted with hot water. The filtrate immediately deposited a crystalline solid which was filtered off and dried *in vacuo*. It was then crystallised from alcohol-benzene mixture, in glistening plates, m.p. 172–73°. [Found : N, 15·62 %. $C_9H_{12}O_2N_2$ requires N, 15·73 %.]

2-Acetylaminobenzylalcohol-5-stibinic acid.—The amino body (8 g.) was dissolved in dilute hydrochloric acid (40 c.c., d. 1·12), cooled to 0° and diazotised with sodium nitrite. To this cooled diazo solution, under vigorous agitation, was added an alkaline solution of sodium antimonite prepared by dissolving antimony trioxide (5 g.) in hydrochloric acid (15 c.c.) and treating with a concentrated solution of caustic soda (30 c.c. 1 : 1). After the vigorous evolution of nitrogen had ceased the liquid was nearly neutralised with dilute sulphuric acid, saturated with carbon dioxide for 15 minutes and filtered. The filtrate was concentrated to about half its volume *in vacuo* over sulphuric acid and salted out when the sodium salt of the stibinic acid separated as a light red flocculent precipitate. This was filtered off, dried *in vacuo* over fused calcium chloride, dissolved in absolute methyl alcohol and precipitated by the addition of dry ether as a colourless amorphous mass. Yield 2 g. The precipitate was filtered and dried *in vacuo*.

over liquid paraffin. [Found: C, 30·23; H, 3·31; N, 3·63; Sb, 30·75; Na, 6·56 %. $C_9H_{11}O_5NSbNa$ requires C, 30·34; H, 3·09; N, 3·91; Sb, 30·9; Na, 6·46 %.]

Properties.—Amorphous mass with a pale pink colour. Decomposes on heating at 240°, without melting. Soluble in water and the free acid is precipitated by acidification and redissolved by alkali. The dried sodium salt is soluble in cold methyl alcohol. Insoluble in dilute mineral acids and other organic solvents.

The calcium or barium salt is precipitated as a white amorphous mass when calcium or barium chloride is added to a solution of the sodium salt.

3-*Nitrobenzylalcohol*-4-*stibinic acid.*—The starting material is 3-nitro-4-aminobenzyl alcohol which was prepared by the method of Fourneau and Lestrange.[4] Owing to the difficulty of diazotising this amine by ordinary method[4] the base (10 g.) was dissolved in alcoholic hydrochloric acid, cooled in ice to 0° and treated with the necessary quantity of amyl nitrite. The solid diazonium chloride was then precipitated by the addition of ether and filtered off in the cold. It was then gradually added to a solution of antimony trichloride prepared by dissolving antimony trioxide (5 g.) in hydrochloric acid (15 c.c., d. 1·18). On stirring a colourless crystalline precipitate separated. This was filtered off and dried carefully on a porous plate. The dry mass was then added in small quantities at a time to pyridine (50 c.c.) and stirred with a glass rod. The colour of the pyridine changed to red and the solid gradually went into solution. Brisk evolution of nitrogen was noticed and the temperature of the liquid went up to about 40–45°. After the addition of the whole of the solid, the solution was warmed on a water-bath to 60°, till evolution of nitrogen had stopped (2 hours). A white solid was found to have separated. This was filtered off and found to be antimony trioxide. The clear liquid of a dark red colour was then diluted with water (500 c.c.) when a light pink gelatanious mass separated. This was filtered off and washed with dilute hydrochloric acid (d. 1·12) to remove antimony trioxide, if any, and then with water till free from acid. As the free stibinic acid is insoluble in organic solvents, it was purified through its sodium salt by precipitating a solution of the sodium salt in water with alcohol (twice). Finally it was dried *in vacuo* over fused calcium chloride (*cf.* Eng. Pat. 313,58 of 1928). [Found: C, 24·51; H, 2·31; N, 3·88; Sb, 34·72 %. $C_7H_7O_6NSbNa$ requires C, 24·42; H, 2·04 N, 4·08; Sb, 34·9 %.]

3-*Aminobenzyl alcohol* 4-*stibinic acid.*—To a solution of the sodium salt described above (8 g.) in *n*-caustic soda (100 c.c.), cooled to 0°, ferrous sulphate (50 g.) in water (100 c.c.) was added slowly with vigorous stirring, the temperature being maintained between 0 and 5°. *n*-Caustic soda (100 c.c.)

was added to the mixture to make it distinctly alkaline and the stirring continued for 4 hours. The sludge of ferric hydroxide was then removed by centrifuging the liquid and the residue was extracted twice with 100 c.c. of 2% caustic soda. The united filtrates were concentrated *in vacuo* and the sodium salt precipitated by the addition of alcohol. The crude sodium salt was then removed by filtration and again dried *in vacuo*. The dried mass was repeatedly extracted with acetone and filtered ; the filtrate was concentrated *in vacuo* and then precipitated by the addition of ether. Finally the precipitated sodium salt was again dried *in vacuo* over calcium chloride—liquid paraffin. [Found : N, 4·25; Sb, 38·15 %. $C_7H_9O_4NSbNa$ requires N, 4·45 ; Sb, 38·22 %.]

Properties.—The sodium salt is a yellowish white amorphous mass, decomposing at 230°, without melting. It is very soluble in water and fairly soluble in acetone. The free stibinic acid is obtained by acidification with dilute acetic acid and dissolves completely in dilute hydrochloric acid. Insoluble calcium salt is precipitated by adding calcium chloride to an aqueous solution of the sodium salt.

The acetyl derivative was prepared by warming the free stibinic acid (1 part) with twice the required quantity of acetic anhydride on a water-bath for a few minutes. On cooling the liquid, a precipitate separates which is filtered off and washed with hot water. The mass was then dissolved in sodium carbonate till just alkaline and again filtered from insoluble impurities, if any. The solution was then concentrated *in vacuo* over caustic soda and saturated with sodium chloride when the sodium salt separated as an amorphous mass. This was filtered off, dried *in vacuo*, dissolved in methyl alcohol and precipitated by the addition of ether, as a light red amorphous mass. [Found : N, 3·72, Sb, 33·56 %. $C_9H_{11}O_5NSbNa$ requires N, 3·93; Sb, 33·7 %.]

The best thanks of the author are due to Prof. Dr. H. K. Sen for placing all the facilities of his laboratory at his disposal.

ON THE MAXIMUM-MODULUS CURVES OF HOLOMORPHIC FUNCTIONS.

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I. Introduction.

Let $f(z)$ be a function holomorphic in a domain D whose boundary is Γ. It is known[1] that $|f(z)|$ cannot attain its upper bound in the interior of D unless it reduces to a constant. If the function is holomorphic on Γ as well there is at least one point on Γ where $|f(z)|$ attains its upper bound in D; this upper bound is also the upper bound of the values of $|f(z)|$ on Γ. Suppose, now that a function $f(z)$ is holomorphic in the circle $|z| \leqslant r$. Let $M(r)$ denote the upper bound or the maximum of $|f(z)|$ in $|z| \leqslant r$. Then there is at least one point on $|z| = r$ where $|f(z)| = M(r)$. We shall call such points M-points. The "maximum-modulus" curve or the "M-curve" is the set of all M-points on $|z| = r$ as r varies, the function remaining holomorphic in the range of variation of r.

1. 1. The object of this paper is to study the nature of this M-curve for a given function. G. Valiron[2] gives an account of the results due to Blumenthal[3] for the case of integral functions. Valiron treats a slightly more general case where he only supposes that $f(z)$ is holomorphic outside a circle $|z| \geqslant R_0$. For the sake of definiteness and simplicity, we suppose throughout this paper that $f(z)$ is holomorphic in the circle $|z| < R$, $f(z)$ having a singular point on $|z| = R$. When $R = \infty$, $f(z)$ is an integral function. We put $z = re^{i\phi}$ and $m = m(r, \phi) = |f(z)|^2$. It is evident that the values of ϕ on $|z| = r$ giving the M-points are the roots of $m(r, \phi) - M^2(r) = 0$. These also satisfy the equation $\frac{\partial m}{\partial \phi} = 0$. We denote by $n(r)$ the number of M-points on $|z| = r$ so that $n(r)$ is the number of real roots, without regard to multiplicity, of the equation $m(r, \phi) - M^2(r) = 0$.

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[1] This is the well-known maximum-modulus principle; for a proof see P. Dienes, "Talyor Series", pp. 149–153.

[2] G. Valiron, *Lectures on Integral Functions*, pp. 25–27.

[3] Blumenthal, *Bull. Soceté Math.*, 1907, t. **31**. This journal is not available to the writer.

1. 2. Valiron proves the following results regarding the function $M(r)$ and the nature of the M-curves :

(a) $M(r)$ can be expressed as a power series of the form given in lemma (6) below in the neighbourhood of any value $r = r_0$;

(b) there are, at most, a finite number of branches of the M-curve in any given annulus.

1. 3. An *apriori* consideration of the nature of the M-curve for a given function involves the following possibilities :—

(α) an arc of the M-curve abuts on to *every* M-point on a given circle $|z| = r_0, 0 < r_0 < R$, *both* from the inside and the outside of the circle $|z| = r_0$;

(β) there are values of r_0 so that $|z| = r_0$ has one or more M-points on it where only one of the possibilities mentioned in (α) occurs ;

(γ) there are values of r_0 such that $|z| = r_0$ contain M-points for which both possibilities mentioned in (α) do not occur ; in this case either

(γ–i) such points are isolated M-points ; or

(γ–ii) there exist sets of M-points *not forming a continuous arc* having an M-point on $|z| = r_0$ as limit point.

1. 4. Valiron's results quoted above do not obviously give an answer to whether any of these possibilities can occur together or alone. So far as I am aware, these cases have not been treated before. In this paper, all these several possibilities are examined and the nature of the values of r for which one or more of these can occur is studied at some length.

1. 5. Lemmas (1)–(3) discuss some elementary properties of $m(r, \phi)$ which are used in the sequel. Lemma (4) is quoted from Valiron ; there is a small defect in his proof of the result contained in (ii) of lemma (2) which is remedied in lemma (6) where Valiron's result on the power-series for $M(r)$ is proved again and a line of argument is developed which is later on used in the proof of theorem (3) and theorem (4). Lemma (5) is introduced to elucidate a not very obvious property of power series with real coefficents.

1. 6. It is first necessary to know whether $n(r)$ can be more than finite for a given value of r. Valiron generally proves that this cannot happen for more than one value of r. In this paper, by assuming that the function is holomorphic at $z = 0$, we are able, in theorem (1), to give the actual form of functions for which such a contingency can happen. They are rational functions of very special types. Though $n(r)$ is finite for each r, we cannot conclude that it is bounded in any closed interval $0 \leqslant r \leqslant r_0$, since $n(r)$ is not continuous ; hence the necessity for theorem (2). Theorem (3) gives a detailed investigation of the nature of the M-curve near $z = 0$, since the usual analysis for $r_0 > 0$ based on lemma (4) is not valid for $z = 0$, because all the

M-points on $|z| = r$, converge to $z = 0$ as $|z| \to 0$. Theorem (4) constitutes, along with theorem (3), the chief result of this paper. It shows that the case (γ–ii) cannot occur. The possibility of (γ–i) is admitted, though I have not been able to prove or disprove the existence of isolated M-points. A classification[4] of the values of r based on theorems (3) and (4) is given in § 4. 2 embodying the possibilities of § 1. 3. Theorems (5)–(7) deal with the nature of the set of values of r for which (α), (β) or (γ) can occur. Theorems (8)–(9) give some properties of $n(r)$. Theorem (10) sums up all the results obtained so far. Theorem (11) illustrates a simple case where the M-curve can be actually located. Some examples to illustrate the various cases are given in the concluding portions.

2. We shall require several preliminary lemmas :—

Lemma (1) : Let $0 \leqslant |z| \leqslant r_0 < R$. The function $m(r, \phi)$ regarded as a function of the two complex variables (r, ϕ) is holomorphic in the region $|r| \leqslant r_0$, $|\phi - \phi_0| < \log R/r_0$, $0 \leqslant \phi_0 \leqslant 2\pi$.

Proof :—We can suppose $\phi_0 = 0$ since otherwise we can deal with $f(ze^{-i\phi_0})$ instead of $f(z)$. We have,

$$f(z) = \sum_{n=0}^{\infty} a_n r^n e^{in\phi} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

Now, $|a_n r^n e^{in\phi}| \leqslant |a_n| r_0^n e^{n|\phi|}$ and the series $\sum_0^{\infty} |a_n| r_0^n e^{n|\phi|}$ converges if $|\phi| < \log R/r_0$ and $e^{n|\phi|}$, when expanded, is a series with positive coefficients. Since $m = f(z)\overline{f(z)}$, we find, from (1), that m can be expressed in the form $\Sigma a_{pq} r^p \phi^q$ in the region considered. Therefore, the theorem is proved.

2. 1. *Lemma* (2) : Let $0 \leqslant r \leqslant r_0 < R$. Then we can find a rectangle $\Gamma(r_0)$ in the ϕ-plane containing the real segment $0 \leqslant \phi \leqslant 2\pi$ in its interior such that $m(r, \phi)$, regarded as a function of ϕ, is holomorphic in the closed rectangle $\Gamma(r_0)$ for each r in $0 \leqslant r \leqslant r_0$.

This is an immediate consequence of lemma (1).

2. 2. *Lemma* (3) : Let $0 < r_0 < R$. We can find an $\eta > 0$ and a rectangle $\Gamma(r_0, \eta)$ containing the segmet $0 \leqslant \phi \leqslant 2\pi$ such that $m(r, \phi) - M^2(r) \neq 0$ on Γ for all r in $(r_0 - \eta, r_0 - \eta)$ while $m(r_0, \phi) - M^2(r_0) = 0$ only for real ϕ in Γ ; and also $m(r, \phi)$ is holomorphic, regarded as a function of ϕ, in and on Γ for each r in $|r - r_0| \leqslant \eta$.

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[4] In this paper, the continuity of the M-curve, rather than its analytic nature, is in question; so far as the latter is concerned, it would follow from the equation of the arcs of M-curves given in the body of the paper that the M-curve is composed of an at most enumerally infinite number of analytic arcs, the points of discontinuity being isolated and finite in number in any circle. $|z| \leqslant r$, $0 \leqslant r < R$.

This is also an immediate consequence of lemma (1) if we remember that $M(r)$ is a continuous function of r.

2. 3. The following lemma has been proved by G. Valiron[5]:

Lemma (4): Let r_0 be a value of r in $0 < r < R$. Let there be a finite number, $\phi_1, \phi_2, \ldots . \phi_p$ of real solutions for the equation $\frac{\partial m}{\partial \phi} = 0$ when $r = r_0$. Then

(i) all the solutions of $\frac{\partial m}{\partial \phi} = 0$ in the neighbourhood of ϕ_k, $k = 1, 2, \ldots p$, are of the form

$$\phi = \phi_k + P[(r - r_0)^{1/\rho}] \quad .. \quad .. \quad .. \quad .. \quad (2)$$

the solutions being valid for values of r in $|r - r_0| \leqslant \eta$. η being a sufficiently small positive number; here $P(u)$ is a power series in u vanishing for $u = 0$ and ρ is a positive integer.

(ii) for each ϕ_k, $k = 1, 2, \ldots . p$, the number of solutions (2) is finite and one at least gives real values for $r \geqslant r_0$ or $r \leqslant r_0$.

(iii) the corresponding values of $m(r, \phi)$ are given by

$$m(r, \phi) = m(r_0, \phi_k) + Q[(r - r_0)^{1/\rho}] \quad .. \quad .. \quad .. \quad (3)$$

where $Q(u)$ is, again, a power series vanishing for $u = 0$ and ρ is the same positive integer as in (2).

2. 4. *Lemma* (5): Let $P(u)$ and $Q(u)$ be two power series with real coefficients. Then, if they are not identical, there is a $\delta > 0$ such that one of them is always greater than the other in $o \leqslant u \leqslant \delta$ and $-\delta \leqslant u \leqslant 0$.

Proof: Let

$$P(u) = a_0 + a_1 u + a_2 u^2 + \ldots \ldots,$$

and

$$Q(u) = b_0 + b_1 u + b_2 u^2 + \ldots \ldots$$

Since $P(u) \not\equiv Q(u)$, there is a least integer k so that $a_k \neq b_k$. We have,

$$\lim_{u \to 0} \frac{P(u) - a_0 - a_1 u - \ldots - a_{k-1} u^{k-1}}{u^k} = a_k,$$

and

$$\lim_{u \to 0} \frac{Q(u) - b_0 - b_1 u - \ldots - b_{k-1} u^{k-1}}{u^k} = b_k.$$

Now $a_0 = b_0, \ldots, a_{k-1} = b_{k-1}$ while $a_k \neq b_k$. Hence the theorem follows for $u > 0$. If $u < 0$, we use $P(-u)$ and $Q(-u)$.

2. 5. *Lemma* (6): Let $0 \leqslant r_0 < R$. There is an $\eta > 0$ such that $M(r)$ can be expressed in the form

$$M(r) = M(r_0) + A[(r - r_0)^{1/\rho}] \quad .. \quad .. \quad .. \quad (4)$$

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[5] G. Valiron, *Lectures on Integral Functions*, pp. 25–27.

for $r_0 \leqslant r \leqslant r_0 + \eta$ and $r_0 - \eta \leqslant r \leqslant r_0$, where A (u) — which might be different for the two intervals—is a power series in u vanishing for $u = 0$ and ρ is a positive integer.

Proof: Consider all the M-points $\phi_1, \ldots . \phi_p$ on $|z| = r_0$. We shall suppose $r_0 \neq 0$; the case $r_0 = 0$ is treated in theorem (3) below. Then ϕ_k, $k = 1, 2, \ldots . p$, satisfies the equation $\frac{\partial m}{\partial \phi} = 0$ for $r = r_0$. In the vicinity of $\phi = \phi_k$, all the roots of $\frac{\partial m}{\partial \phi} = 0$ are given by expressions of form (2) and by lemma (4) (ii), there is one solution which gives real values for $r \geqslant r_0$ or $r \leqslant r_0$. We shall first prove that for $r = r_0$ there is at least one ϕ_k for which a solution of form (2) exists which is real for $r \geqslant r_0$ and at least one for which it is real for $r \leqslant r_0$. Consider the case $r \geqslant r_0$. There are M-points on $|z| = r \to r_0 + 0$ and these have at least one limit point on $|z| = r_0$ which must be one of the points ϕ_k since M (r) is a continuous function of r. Let $\{r_n\}$, $r_n \to r_0 + 0$, be a sequence of values of r such that $|z| = r_n$ has an M-point on it tending to the point ϕ_k on $|z| = r_0$ as $r_n \to r_0 + 0$. We can suppose these M-points to lie on one of the curves (2) issuing outward from ϕ_k. When $r = r_n$ in (2), the corresponding ϕ is real ; and since $\{r_n\}$ is more than a finite sequence of values of r which renders (2) real, the solution (2) on which these M-points lie must give real values for all $r \geqslant r_0$ in a sufficiently small interval $r_0 \leqslant r \leqslant r_0 + \eta$ for which such a solution is valid. A similar reasoning holds for $r \leqslant r_0$.

Now, consider all those points ϕ_k on $|z| = r_0$ where there is a real solution (2) for $r \geqslant r_0$ and consider all such solutions at ϕ_k and this for all such ϕ_k. When these are substituted in $m\ (r, \phi)$ we get a finite number of power series of form (3) and by the repeated application of lemma (5) we can find an $\eta > 0$ such that there is one power series among these which is not less than the rest in the interval $r_0 \leqslant r \leqslant r_0 + \eta$. This power series evidently gives the value of $M^2(r)$ and $M(r)$ can be written in the form (4) in virtue of (3). This completes the proof of the lemma for $r \geqslant r_0$. A similar argument holds for $r \leqslant r_0$.

3. We now proceed to prove the theorems of this paper.

THEOREM (1) :—Let $0 \leqslant r_0 < R$. Then $n\ (r_0)$ is finite unless $f(z)$ is of the form

$$f(z) = C \prod_{k=1}^{n} \frac{z - a_k}{r_0 - \frac{\bar{a}_k z}{r_0}} \qquad \ldots \ldots \ldots \ldots \qquad (5)$$

where $|a_k| < r_0$, $k = 1, 2, \ldots . n$ and C is a constant. If there be two values r_0 and r_1 for which $n\ (r)$ is more than finite, then $f(z) = Cz^n$. If $f(z)$ is

an integral function and $n(r)$ is not finite for some r then $f(z) = Cz^n$. In these two cases $|f(z)| = M(r)$ on every circle $|z| = r$.

Proof: By definition, $n(r_0)$ is the number of real roots (counted without regard to multiplicity) of $m(r_0, \phi) - M^2(r_0) = 0$ in $0 \leqslant \phi \leqslant 2\pi$. Since $m(r_0, \phi)$ is holomorphic in ϕ in the rectangle $\Gamma(r_0)$ of lemma (2), $n(r_0)$ is more than finite if and only if $m(r_0, \phi) - M^2(r_0) \equiv 0$. In this case, $|f(z)| = M(r_0)$ on $|z| = r_0$. If $f(z)$ has a zero on $|z| = r_0$, $f(z) \equiv 0$. If $f(z)$ has no zeros in $|z| \leqslant r_0$, we find, by applying the maximum modulus principle to $\frac{1}{f(z)}$ that $|f(z)| \equiv M(r_0)$ in $|z| \leqslant r_0$ and therefore $f(z) = C$, a constant. Now suppose $f(z)$ has n zeros $a_1 \ldots, a_n$ in $|z| < r_0$. Let

$$g(z) = \prod_{k=1}^{n} \frac{z - a_k}{r_0 - \frac{a_k z}{r_0}}.$$

We find $|g(z)| = 1$ on $|z| = r_0$. Therefore $\left|\frac{f(z)}{g(z)}\right| = M(r_0)$ on $|z| = r_0$ while $\frac{f(z)}{g(z)}$ is holomorphic and has no zeros in $|z| \leqslant r_0$. Therefore, by what has been already proved, $f(z) = cg(z)$. If $f(z) =$ an integral function, it can have the form (5) if and only if $a_k = 0$, $k = 1, 2, \ldots n$, since otherwise, it will have a finite pole. Now let $n(r)$ be infinite for two values r_0 and r_1, where $r_0 < r_1$, say. Then $f(z)$ is of form (5) and so cannot have other zeros than $a_1, \ldots a_n$. Therefore we must have

$$C_0 \prod_{k=1}^{n} \frac{z - a_k}{r_0 - \frac{a_k z}{r_0}} \equiv C_1 \prod_{k=1}^{n} \frac{z - a_k}{r_0 - \frac{a_k z}{r_1}}.$$

From this relation we get, for $z = 0$, $\frac{C_0}{r_0^n} = \frac{C_1}{r_1^n}$ and therefore,

$$\prod_{k=1}^{n}\left(\frac{1}{z} - \frac{a_k}{r_0^2}\right) = \prod_{k=1}^{n}\left(\frac{1}{z} - \frac{a_k}{r_1^2}\right)$$

which can hold only if $a_k = 0$, $k = 1, 2, \ldots . n$ since $r_0 \neq r_1$. Therefore the theorem is proved.

3. 1. We suppose, in what follows, that $f(z)$ is not of the exceptional form (5), though all the results hold for values of r in $0 \leqslant r < r_0$ and $r_0 < r < R$ in case there happens to be only one r_0 for which $n(r_0)$ is infinite.

3. 2. THEOREM (2) :—Let $0 \leqslant r \leqslant r_0 < R$. Then $n(r)$ has a finite upper bound as r varies in $0 \leqslant r \leqslant r_0$, the upper bound depending on $f(z)$ and r_0.

Proof: We shall prove in theorem (3) that there is a $\delta > 0$ and a finite integer k such that $n(r) = k$, $0 < r \leqslant \delta$. Now consider the interval $\delta \leqslant r \leqslant r_0$. $n(r)$ is the number of real zeros of the holomorphic function $m(r, \phi) - M^2(r)$ in the rectangle $\Gamma(r_0)$ of lemma (2). As r varies in $\delta \leqslant r \leqslant r_0$, the functions $\{m(r, \phi) - M^2(r)\}$ constitute a uniformly bounded family of functions holomorphic in $\Gamma(r_0)$ and so constitute a normal family.[6] The limit functions of the family belong to the family and so are not identically zero since $n(r)$ is finite for all r considered. Therefore by a well-known property[6] of a normal family, the number of zeros in $\Gamma(r_0)$ and therefore $n(r)$ has a finite upper bound as r varies in $\delta \leqslant r \leqslant r_0$. This completes the proof of the theorem.

4. The following two theorems constitute the fundamental results of this paper.

THEOREM (3) :—There is a $\delta > 0$ such that $n(r) = k$, a constant finite integer, for $0 < r \leqslant \delta$ and there are k branches of the M-curve issuing from the origin, the equations of these being of form (2) with $\rho = 1$. The integer k cannot exceed $2p - 1$ where p is the first integer such that $f^{(p)}(0) \neq 0$.

Proof: We can suppose, without loss of generality, that $f(0) = 1$; otherwise we can deal with $\frac{f(z)}{az^\lambda}$ which would satisfy the specified condition by proper choice of a and λ and which has exactly the same M-curve as $f(z)$. Therefore we can write

$$f(z) = 1 + a_p z^p + \ldots . , \quad a_p \neq 0, p \geqslant 1.$$

So we have,

$$m = (1 + a_p r^p e^{pi\phi} + \ldots .)\ (1 + \bar{a}_p r^p e^{-pi\phi} + \ldots .) ;$$

so that

$$\frac{\partial m}{\partial \phi} = ipr^p \left\{ a_p e^{pi\phi} - \bar{a}_p e^{-pi\phi} + r\chi(r, \phi) \right\}$$

where $\chi(r, \phi)$ is a power series in (r, ϕ) bounded in the neighbourhood of $r = 0$ for $0 \leqslant \phi \leqslant 2\pi$. Let $u(r, \phi)$ denote the expression in the bracket. It can vanish, for $r = 0$, only for the $2p$ values of ϕ given by $e^{2pi\phi} = \frac{\bar{a}_p}{a_p}$. Let ϕ_k be one of these values. Then $\left(\frac{\partial u}{\partial \phi}\right)_{(0, \phi_k)} = 2ip\ \bar{a}_p e^{pi\phi_k} \neq 0$. Therefore $\frac{\partial m}{\partial \phi} = 0$ has a unique solution of the form (2) with $\rho = 1$ in

[6] For the definition of a normal family and the properties used here, see P. Montel, *Familles normales de functions analytiques*, pp. 21, 36.

the neighbourhood of $\phi = \phi_k$, $k = 1, 2, \ldots\ldots 2p$, given by $e^{2pi\phi} = \frac{\bar{a}_p}{a_p}$. The solution (2) is valid for $0 < r \leqslant \delta$ and on $|z| = r$ in this interval, there are $2p$ points where $\frac{\partial m}{\partial \phi} = 0$. Since $f(0) = 1 \neq 0$, one of these points corresponds to the minimum of $|f(z)|$ in $|z| \leqslant r$ and therefore $n(r) \not> 2p-1$ if δ is sufficiently small. Now we can repeat the argument of lemma (6) and conclude that

(i) $M^2(r)$ can be written in the form

$$M^2(r) = M(0) + A(r) \quad .. \quad .. \quad .. \quad .. \quad (6)$$

which is valid in some interval $0 \leqslant r \leqslant \delta$;

(ii) there is an integer $k \not> 2p-1$ such that $n(r) = k$, $0 < r \leqslant \delta$;

(iii) there are k branches of the M-curve issuing from the origin whose equation is of form (2) with $\rho = 1$;

(iv) the tangents to these curves at $r = 0$ are the lines $\phi = \phi_k$, ϕ_k being a root of $e^{2pi\phi} = \frac{\bar{a}_p}{a_p}$ such that the corresponding solution (2) when substituted in (3) gives (6); and

(v) the angle between any two of these tangents is a multiple of $\frac{\pi}{p}$.

This completes the proof of the theorem.

4. 1. THEOREM (4):—Let $0 < r < R$. Let $z_k(r_0)$, $k = 1, 2, \ldots . p$, $p = n(r_0)$, be the M-points on $|z| = r_0$. If $z_k(r_0)$ is not an isolated M-point, there is a branch of the M-curve whose equation is of form (2) abutting on to z_k from inside *or* outside $|z| = r_0$.

Note.—By an isolated M-point z_k is meant one such that in a sufficiently small circle round z_k there is no M-point except z_k itself.

Proof: Let z_k be an M-point on $|z| = r_0$ which is not isolated. By lemma (4), there are a finite number of real curves of the form (2) which satisfy $\frac{\partial m}{\partial \phi} = 0$ and abut on to z_k from inside or outside the circle $|z| = r_0$. By hypothesis, there is a sequence $\{r_n\}$ of values of r and a corresponding sequence $\{z(r_n)\}$ of M-points such that $r_n \to r_0$ and $z(r_n) \to z_k(r_0)$. By restricting ourselves to a sub-sequence, if necessary, we can suppose that $\{z(r_n)\}$, for $n \geqslant n_o$, lie on one of the curves (2) abutting on to z_k from inside *or* outside as the case may be.[7] When $r = r_n$ in the equation (2) of this

[7] It might happen that there is no sequence of M-points tending to z_k from outside in which case there must be a sequence tending to z_k from inside, since z_k is not isolated and *vice versa*.

curve, the corresponding value of ϕ gives $m(r, \phi)$ the value $M^2(r_n)$ and therefore equal to the square of the series on the right side of (4) when $r = r_n$. But the substitution of the equation of the curve in $m(r, \phi)$ gives a power series (3) whose positive square root is again a power series P_1 which equals (4) when $r = r_n$, $n \geqslant n_0$. Therefore, the power series P_1 is identical with (4) for *all* values of r in a certain neighbourhood of r_0 to the left or to the right as the case may be. Therefore, the curve on which $z(r_n)$ lie is a branch of the M-curve; its equation is of form (2) and it abuts on the z_k from inside or outside as the case may be.

4. 2. Theorems (3) and (4) suggest the following classification of the values of r in $0 \leqslant r < R$ with respect to the M-points. Let $z_k\ (r_0)$, $k = 1, 2, \ldots p$, $p = n(r_0)$, be the M-points on $-\ |z| = r_0$. Let $dr_0\ (z_k, r)$ be the least distance of $z_k\ (r_0)$ from the M-points on $|z| = r$. We shall say that

(i) $r = r_0$ is a regular point when $d_{r0}(z_k, r) \to 0$ as $r \to r_0 + 0$ *or* $r \to r_0 - 0$ and this happens for *all* $k = 1, 2, \ldots p$;

(ii) $r = r_0$ is perfectly regular when $d_{r0}\ (z_k, r) \to 0$ as $r \to r_0$, for *all* $k = 1, 2, \ldots p$. It is evident that r_0 is regular if it is perfectly regular. It is evident from theorem (3) that all values of r in $0 < r \leqslant \delta/2$ are perfectly regular. Since we do not consider negative values of r, we agree to consider $r = 0$ as a perfectly regular point;

(iii) $r = r_0$ is a singular point in case there is at least one M-point on $|z| = r_0$ for which (i) is not true. It follows from theorem (4) that $r = r_0$ can be singular if and only if there is an isolated M-point on $|z| = r_0$.

4. 3. With the classification adopted above, we can restate theorems (3) and (4) as follows :—

THEOREM (5) :—If $r = r_0$ is a regular point, there is a branch of the M-curve whose equation is of form (2) abutting on to *every* M-point on $|z| = r_0$ from inside *or* outside the circle $|z| = r_0$. If $r = r_0$ is perfectly regular, there is a branch of the M-curve with equation (2) abutting on to *every* M-point on $|z| = r_0$ both from inside *and* outside the circle $|z| = r_0$. There is a $\lambda > 0$ such that all r in $0 \leqslant r \leqslant \lambda$ are perfectly regular.

5. We now proceed to the examination of the singular and non-perfectly regular values of r. The following theorem gives the essential information on this point.

THEOREM (6) :—Let $0 \leqslant r_0 < R$. There is an $\eta > 0$ such that all r in $0 < |r - r_0| \leqslant \eta$ are perfectly regular. No hypothesis is made on $r = r_0$ itself.

Proof: It is evident from the proofs of theorems (3) and (4) that there is at least one M-point on $|z| = r_0$ from which a branch of the M-curve proceeds outward and one from which a branch proceeds inward. Consider all those points on $|z| = r_0$ from which branches of the M-curve issue outward and let δ be the least distance between these points. If circles of radius $\delta/4$ be drawn round these points, the circles will be non-overlapping and there is a $\delta_1 > 0$ such that all the M-points on $|z| = r$ for $r_0 < r \leqslant r_0 + \delta_1$, lie inside these circles. Since the M-curves are composed of arcs whose equation is of form (2), it is evident that all r in $r_0 < r \leqslant r_0 + \delta_1/2$ are perfectly regular since any M-point on $|z| = r$, for these values of r, lies on an arc of the M-curve issuing from a point on $|z| = r_0$ and proceeding continuously up to a point on $|z| = r_0 + \delta_1$. A similar reasoning holds for values of $r < r_0$. For $r_0 = 0$, we need consider only values of $r > 0$ and use theorem (3). This completes the proof of the theorem.

5. 1. The following theorem is an immediate corollary of theorem (6):

THEOREM (7):—(i) The number of singular points in $0 \leqslant r \leqslant r_0$, $r_0 < R$, is finite; the totality of the singular points constitute an at most enumerably infinite isolated set with the sole possible limit point $r = R$;

(ii) the points which are regular but not perfectly regular have exactly the same property as in (i);

(iii) the perfectly regular values of r constitute a set of finite or enumerably infinite set of open intervals whose end-points are the points of (i) and (ii) in case the latter exist. The interval nearest the origin is closed at $r = 0$.

6. We shall now derive some properties of $n(r)$ for perfectly regular points.

THEOREM (8):—Let $r = r_0$ be a perfectly regular point. There is an $\eta > 0$ such that $n(r) \geqslant n(r_0)$ for all r in $|r - r_0| \leqslant \eta$.

Proof: Let δ be the minimum distance between the M-points on $|z| = r_0$. The circles round these M-points with radius $\delta/4$ are non-overlapping. By the definition of a perfectly regular point, there is an $\eta > 0$ such that for all r in $|r - r_0| \leqslant \eta$, there is an M-point on $|z| = r$ in each of these circles: So $n(r) \geqslant n(r_0)$.

6. 1. THEOREM (9):—Let $r_1 \leqslant r \leqslant r_2$ be a closed interval of perfectly regular points, Let E (r) denote the set of values of r for which $m(r, \phi) - M^2(r) = 0$, $\dfrac{\partial^2 m}{\partial \phi^2} = 0$, simultaneously for a real ϕ. Let (r_1, r_2) contain no point of E. Then $n(r)$ is a constant in (r_1, r_2).

Proof: Let $r = r_0$ be a point in the closed interval (r_1, r_2). For $r = r_0$, $\dfrac{\partial^2 m}{\partial \phi^2} \neq 0$ when $m(r_0, \phi) - M^2(r_0) = 0$, ϕ being real. Hence, the real roots

of the latter equation are double roots. Therefore in the rectangle $\Gamma(r_0, \eta)$ of lemma (3), there are $2n(r_0)$ zeros of the holomorphic function $m(r_0, \phi) - M^2(r_0)$. By lemma (2), $m(r, \phi) - M^2(r) \neq 0$ on Γ if $|r - r_0| \leqslant \eta$. Therefore, the number of roots of $m(r, \phi) - M^2(r) = 0$ in Γ for these values of r is given by the integral

$$\frac{1}{2\pi i} \int_{\Gamma(r_0, \eta)} \frac{\frac{\partial m}{\partial \phi}}{m(r, \phi) - M^2(r)} d\phi \quad .. \quad .. \quad .. \quad .. \quad (7)$$

which, being a continuous function of r, is equal to $2n(r_0)$ when $|r - r_0| \leqslant \eta$, η being sufficiently small. Evidently $2n(r)$ is not greater than the value of (7) and therefore $n(r) \leqslant n(r_0)$. But $n(r) \geqslant n(r_0)$ if η is small enough. Hence there is a $\delta > 0$ such that $n(r) = n(r_0)$ for $|r - r_0| \leqslant \delta$, that is $n(r)$ is continuous at $r = r_0$. But $n(r)$ is an integer and being continuous at all points of (r_1, r_2) must, therefore, be a constant. So the theorem is proved.

7. We can now sum up the results obtained so far in the following theorem :

THEOREM (10) :—Omitting an at most enumerably infinite isolated set of values of r in $0 \leqslant r < R$, the sole possible limiting point of the set being $r = R$, we find that :

(i) there is a branch of the M-curve whose equation is of form (2) [$\rho = 1$ when $r = 0$] abutting on to *every* M-point on $|z| = r$ both from inside and outside the circle $|z| = r$;

(ii) the set of values of r in (i) constitute a set of non-overlapping open intervals whose end-points are the omitted points and $n(r)$ is constant in each of these intervals if it contains no point of E. The interval nearest the origin is closed at $r = 0$ and there is a $\lambda > 0$ such that $n(r) = k$ in $0 < r \leqslant \lambda$, k being a finite positive integer $\not> 2p - 1$ where p is the least integer so that $f^p(0) \neq 0$.

7. 1. The following theorem gives a general class of functions whose M-curve is composed of a finite number of straight lines through the origin.

THEOREM (11) :—Let

$$f(z) = a_0 + a_{p_1} z^{p_1} + a_{p_2} z^{p_2} + \ldots, \quad .. \quad .. \quad .. \quad (8)$$

where $a_{p_k} \neq 0$, a_0 being supposed real and positive, without loss of generality. Let there be an r_0 so that $M(r_0) = \Sigma |a_{p_k}| r_0^{p_k}$.

Then

(i) $M(r) = |\Sigma a_k| r^{p_k}$ for all, $0 < r < R$ and the M-curve is composed of one or more straight lines through $z = 0$;

(ii) if there be more than one line, there is an integer $d > 1$ which is the G.C.M. of $(p_1, p_2, \ldots)$ and there are exactly d straight lines forming the M-curve and the angle between consecutive lines is $\frac{2\pi}{d}$.

Proof: Let $z_0 = r_0 e^{i\phi_0}$ be an M-point on $|z| = r_0$. Then we have,

$$|\Sigma a_{p_k} r_0^{p_k} e^{p_k i\phi}| = \Sigma |a_{p_k}| r_0^{p_k} \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

But, if $a \neq 0$, $b \neq 0, \ldots\ldots$ we can have $|\Sigma a| = \Sigma |a|$ if and only if $\frac{a}{|a|} = \frac{b}{|b|} \ldots\ldots$ So, if $a_{p_k} = |a_{p_k}| e^{i\theta_{p_k}}$, we get from (9),

$$p_k \phi_0 + \theta_{p_k} = 2h_k\pi_{p_k}$$

where h_k are integers. Therefore,

$$|\Sigma a_{p_k} r^{p_k} e^{ip_k\phi_0}| = \Sigma |a_{p_k}| r^{p_k} = M(r) \quad \ldots \quad \ldots \quad (10)$$

and so the line $\phi = \phi_0$ is part of the M-curve. If there be another, let $\phi = \phi_1 < \phi_0$ be its equation. Then from (10) we have supposing $0 \leqslant \phi_0 < 2\pi$, $0 \leqslant \phi_1 < 2\pi$,

$$p_k(\phi_1 - \phi_0) = 2\lambda_k\pi$$

or,

$$\frac{\lambda_k}{p_k} = \frac{\phi_1 - \phi_0}{2\pi} = \frac{\lambda}{\mu} < 1, \text{ say, } \ldots \quad \ldots \quad \ldots \quad \ldots \quad (12)$$

where $\frac{\lambda}{\mu}$ is in its lowest form. Hence $\mu > 1$ divides all p_k and if d is the G.C.M. of $p_1, p_2 \ldots$, $d \geqslant \mu > 1$. From (12) we conclude that stright lines making angles $\frac{2k\pi}{d}$, $k = 0, 1, \ldots . d - 1$, with $\phi = \phi_0$ also form part of the M-curve and there is no other since its inclination ϕ_1 must satisfy (12). So the theorem is proved.

7. 2. I have not been able to find an example of $f(z)$ with an isolated M-point nor to disprove the existence of such points. An example where $\overline{\lim_{r \to R}} n(r) = \infty$ also seems difficult. Illustrations for the remaining cases are known and are given below in § 7·3.

7. 3. (i) Let $f(z) = (z - 1)(z + 2)$. Here

$$m = (r^2 - 2r\cos\phi + 1)(r^2 + 4r\cos\phi + 4)$$

and the M-curve is composed of 3 parts :

(*a*) $\phi = \pi$, $0 \leqslant r \leqslant 3\sqrt{2} - 4$; $M(r) = 2 + r - r^2$;

(*b*) the circle $r^2 - 8r\cos\phi - 2 = 0$ with centre $r = 4$, $\phi = 0$ and radius $3\sqrt{2}$; r varies in $3\sqrt{2} - 4 \leqslant r \leqslant 3\sqrt{2} + 4$ and $M(r) = \frac{3}{2\sqrt{2}}(r^2 + 2)$;

(*c*) $\phi = 0$, $r \geqslant 3\sqrt{2} - 4$; $M(r) = r^2 + r - 2$.

Here $n(r) = 1$, $0 \leqslant r \leqslant 3\sqrt{2} - 4$; $n(r) = 2$, $3\sqrt{2} - 4 < r < 3\sqrt{2} + 4$; and $n(r) = 1$, $r \geqslant 3\sqrt{2} + 4$. We find $\frac{\partial^2 m}{\partial \phi^2} = 0$ at the points ($r = 3\sqrt{2} - 4$, $\phi = \pi$) and ($r = 3\sqrt{2} + 4$, $\phi = 0$) and $n(r)$ changes from 1 to 2 and 2 to 1 respectively at these points; all values of r are perfectly regular.

(ii) Hardy[8] has shown that for the function

$$f(z) = e^{e^{z^2}} + \sin z$$

there is an r_0 such that for $r \geqslant r_0$, $M(r) = e^{e^{r^2}} + |\sin r|$ and the M-curve is given by

(α) $\phi = 0$, $2k\pi \leqslant r < (2k + 1)\pi$, $k = \pm k_0, \pm (k_0 + 1), \ldots\ldots$ where $k_0\pi \geqslant r_0$;

(β) $\phi = \pi$, $(2k + 1)\pi < r \leqslant (2k + 2)\pi$, $k = \pm k_0, \pm (k_0 + 1) \ldots\ldots$ Here, all the points $r = k\pi$, $r < r_0$, are regular but not perfectly regular points. All other values of $r \geqslant r_0$ are perfectly regular. Also $n(r) = 1$, $r \neq k\pi$, $r \geqslant r_0$ while $n(k\pi) = 2$ though $\frac{\partial^2 m}{\partial \phi^2} \neq 0$ for these M-points. Therefore $n(r)$ can change value at points, not perfectly regular without $\frac{\partial^2 m}{\partial \phi^2}$ being zero.

Additional Note.

Dr. Vaidyanathaswami has kindly pointed out that the inequality $k \not> 2p - 1$ in theorem (3) could be replaced by the sharper result $k \not> p$. To prove this we note that $m(r, \phi)$ for a given r is a continuous differentiable real function of ϕ, $0 \leqslant \phi \leqslant 2\pi$ and if there be k M-points for some r there are also k points where $m(r, \phi)$ has minima, local or absolute. Hence from the proof of theorem (3) $2k \not> 2p$ or $k \not> p$.

[8] Hardy, "The maximum modulus of an integral function," *Quarterly J. of Math.*, 1909, pp. 1 *et seq.*

AN OPTICAL INVESTIGATION OF SOME INDIAN OILS.

I. Depolarisation of the Scattered Light.

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1. *Introduction.*

It is now well known that striking alterations are produced in the intensity and polarisation characters of the scattered light as the particles grow large in size, and ellipsoidal in shape. If the particles are small and spherical, the laws of scattering tell us that the light scattered in a transverse direction is always perfectly polarised irrespective of the state of polarisation of the incident light. On the other hand, the existence of particles which are either large in size or non-spherical in shape or both causes a depolarisation in accordance with the following table taken from a recent paper by Krishnan (1934).

Nature of particle	Incident light unpolarised	Incident light polarised with electric vector vertical	Incident light polarised with electric vector horizontal
Spherical particles of finite size	$\rho_u < 1$	$\rho_v = 0$	$\rho_h = \infty$
Small ellipsoidal particles	$\rho_u = \frac{2\rho_v}{\rho_v+1} < 1$	$\rho_v < 1$	$\rho_h = 1$
Ellipsoidal particles of finite size	$\rho_u < 1$	$\rho_v < 1$	$\rho_h > 1$

ρ_h, ρ_u and ρ_v respectively signify the depolarisation factors when the incident light is horizontally polarised, unpolarised and vertically polarised. Besides such depolarisation characters, a definite asymmetry of scattering may also be expected when the particles are large in size, the scattered beam being more intense in the forward direction than in the backward direction. Thus, either a study of the distribution of intensity of the scattered light or its state of polarisation under different conditions furnishes us with a method of studying the size and shape of the scattering centres.

This latter method has recently been extensively applied by Subbaramayya (1935) and Krishnan (1935) to a number of interesting cases.

Subbaramayya measured ρ_u, ρ_v and ρ_h in the case of many colloidal suspensions and found an appreciable value for ρ_v and that ρ_h in all cases was notably different from 100% thus showing that the colloidal particles were ellipsoidal in shape and large in size compared with the wave-length of light. Krishnan (1935) examined a number of binary liquid mixtures, optical glasses and a few pure liquids. He measured ρ_h under different conditions and definitely established the existence of large clusters of molecules in optical glasses and binary mixtures. He was also of the opinion that such groups are present even in pure liquids like formic and acetic acids. This is somewhat surprising.

It is proposed in this paper to extend this optical method of determining the size and shape of the molecular clusters to the case of some vegetable oils. Some of these may, on account of their high viscosity, be expected to reveal interesting features. Incidentally their depolarisation factors, which were not hitherto available, have been obtained. Krishnan's experiments in the case of formic and acetic acids are also repeated.

2. *Experimental Arrangements.*

All observations are made inside a dark cabin. A Zeiss biotar lens is fitted into one of the walls of the cabin at a convenient height and light from a carbon arc is focussed by means of the biotar lens on to a rectangular cell containing the pure dust-free liquid. The outside of the rectangular glass cell is painted black, leaving small apertures in the sides of the cell for the incident and transversely scattered light to pass through. The distance between the glass cell and the lens is so adjusted that the narrow pencil of light coming out of the lens is brought to a focus at the middle of the cell. Observations are made at the focus and the error due to convergence comes out as 0·8.* This is very small in comparison with the observed depolarisation factors. A double-image prism is introduced into the path of the incident beam, so that the vertical and horizontal components are widely separated and in such a manner that the upper image corresponds to the vertical vibrations. The transversely scattered light is examined through another double-image prism and a nicol. Great care has been taken to see that the double-image prisms, the nicol, the glass cell and the biotar lens are all in the same horizontal plane and also that the incident beam entered the cell normally and that the transversely scattered beam is observed normally. Any slight departure from the above conditions is found to result in spurious

* The convergence correction, according to Ananthakrishnan (1935), is given by $\frac{\Omega^2}{2}$ where Ω is the semi-angle of convergence. In these experiments the semi-angle is ⅛ and hence the convergence correction comes out to be 0.8 per cent., which has to be subtracted from the values of ρ given in Table I.

effects. In order to test whether the arrangements are proper or not, benzene is examined as a test case. The arrangements are accepted only when benzene exhibited a ρ_h equal to 100%. Under such conditions, five different oils and formic and acetic acids have been examined and ρ_h measured in all the cases. This is achieved by interposing a suitable stop in the path of the incident beam, so as to cut off the vertical component.

In all these cases the depolarisation with incident light unpolarised (*i.e.*, without the double-image prism in the path of the incident beam) is also measured using alternately the full light of the arc and only a small portion of it in the red region of the spectrum for incidence. In the former case, very large values of ρ_u are obtained showing an admixture of a lot of fluorescence with the genuinely scattered light. In order to eliminate fluorescence and obtain the true depolarisation factor, a dark red glass is interposed in the path of the incident beam and the depolarisation values are again measured.

3. *Purification of the Oils.*

The oils examined here are all Indian vegetable oils, except olive oil. The oils as got from the market are deeply coloured and turbid presumably due to the presence of some insoluble free fatty material and suspended particles. With a view to obtain them in a state suitable for optical purposes, all the oils have been subjected to the following uniform method of purification. The refining consisted of (i) removal of the free fatty acids, (ii) decolourisation of the oil and (iii) removal of dust and other suspended particles.

Removal of free fatty acids.—The oil is at first washed well with an equal amount of distilled water, so that soluble fats are dissolved by it. Calculated amounts of sodium hydroxide solution are added to the oils thus washed and the mixture is well shaken. The caustic soda forms a soap with the free fat and on adding a little alcohol, the soapy matter separates out. The clear oil is removed by means of a separating funnel. The alcohol dissolved in the oil has been removed by fractional distillation under reduced pressure.

Bleaching the oil.—Animal charcoal is heated strongly in a china dish and added to the oil to the extent of about 2% of its weight. The oil is stirred well and set aside for 24 hours. It is then filtered three times through filter paper having very fine pores. Except olive oil, all the other oils could be bleached by charging the oil once with animal charcoal. Olive oil, however, had to be treated with animal charcoal twice.

Removing dust and other suspended particles.—Fuller's earth, previously heated strongly, is added to the oil to the extent of about 2% of its weight. The oil is kept stirred for about half an hour at a temperature of 60° C. The oil is then allowed to settle and after 24 hours, it is filtered three times through

fine filter paper. Thus the oil is rendered dust-free. Fuller's earth is used as it has got the specific property of removing all finely suspended particles.

All the oils have been subjected to this treatment, except olive and castor oils. Olive oil (B. C. P. Works) is purchased from the market and is labelled "free from fatty acids" and so it is subjected to the latter two processes only. In the case of castor oil, a sample of colourless and pure oil available in the market is taken and treated with Fuller's earth alone.

4. Results.

The results obtained are given in Table I.

TABLE I.

Depolarisation of the light scattered by vegetable oils and formic and acetic acids.

Substance	Colour of the track	$\rho_h \times 100$	$\rho_u \times 100$ full light	$\rho_u \times 100$ red light
Gingelli oil	reddish	70	16·1	12·7
Cocoanut oil	blue	100	69·9	42·2
Groundnut oil	blue	100	62·5	35·5
Castor oil	blue	100	57·5	46·0
Olive oil	whitish blue	100	41·8	20·9
Formic acid	blue	100	43·0	38·3
Acetic acid	blue	100	....	....

The refractive indices of the oils for two wave-lengths, namely, λ4358 and λ5460 have also been measured by means of a Pulfrich Refractometer, with a view to see if there is any correlation between the degree of dispersion and the depolarisation factor. The results are given in Table II.

TABLE II.

Refractive indices of oils.

Name of the oil	$\mu(e)$ (5460)	$\mu(g)$ (4358)	$\mu_g - \mu_e$
Gingelli oil	1·47144	1·48128	·00984
Cocoanut oil	1·45434	1·46244	·00810
Groundnut oil	1·46837	1·47755	·00918
Castor oil	1·47763	1·48715	·00952
Olive oil	1·46807	1·47715	·00908

5. Discussion of the Results.

The values of ρ_h for formic and acetic acids obtained by the author and given in Table I, show that these liquids are quite normal. These results

do not support the view that aggregates are present in pure liquids. This is in contradiction to Krishnan's conclusions. The values of ρ_h for the oils show that similar conclusions hold good even here except in the case of gingelli oil. It may be remarked here that castor oil at first showed a ρ_h which was sensibly different from 100 but on careful purification, this result has been found to be spurious. The fact that in the case of gingelli oil, suspended particles could not be removed completely and that the track of light was distinctly reddish in colour in spite of repeated purifications shows that nothing definite can be said in regard to the existence or otherwise of large molecular clusters in this oil.

The refractive index measurements are in agreement with the figures already available for these oils in the literature (Paranjpe and Deshpande, 1935) and show that the dispersion of refractive index is more or less the same for all the oils studied here.

Further optical investigation with these and other oils is in progress and will form the subject-matter of some following communications.

6. *Summary.*

Five different oils have been refined by the standard methods and rendered suitable for optical investigations. The depolarisation of the light scattered by the oils so purified has been measured using horizontally polarised and unpolarised incident light. In the latter case the depolarisation values are also obtained by interposing a dark red glass in the path of the incident beam. With the exception of gingelli oil, all oils exhibited a depolarisation factor of 100% when the incident light is horizontally polarised. In this respect the behaviour of these oils is similar to that obtained in pure liquids. In gingelli oil a different value is obtained but much significance is not attached to this result. Formic and acetic acids also show a depolarisation of 100% under these conditions in contradiction to the results reported earlier by Krishnan. Depolarisation factors of 12·7, 42·2, 35·5, 46·0 and 20·9 when expressed as percentages have been obtained for gingelli, cocoanut, groundnut, castor and olive oils respectively with incident red light.

The author wishes to express his gratefulness to Mr. S. Bhagavantam, the Head of the Physics Department, for his very valuable and kind guidance during the course of this work.

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ON NON-SPHERICAL NATURE OF COLLOIDAL PARTICLES IN RELATION TO THE FORMATION OF JELLY STRUCTURE.

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1. Introduction.

The non-spherical colloidal particles are known to orient themselves under the action of mechanical, electrical and magnetic strains. It was observed by Maxwell[1] that a viscous liquid during the course of flow exhibits bi-refringence and the extensive work of Vörlander and Walter[2] showed that this sort of mechanical or stream double refraction is observed in a large number of liquids possessing only a moderate viscosity. Kundt[3] for the first time studied the Maxwell effect in the case of gelatine which forms a lyophilic suspension. Similar suspensoids were also investigated for the effect by Bernatzki[4] and Bjornstahl,[5] Quincke,[6] Tiere,[7] Freundlich and co-workers[8] and also Graffi[9] obtained a positive stream double refraction with an iron oxide sol. Bjornstahl obtained negative double refraction with gold sols. Zocher[10] investigated a number of dyestuffs like benzopurpurin, cotton yellow and aniline blue, and the vanadium pentoxide sol has been extensively studied by Freundlich, Zocher and others.[11]

The phenomenon of electric birefringence in the case of colloids has not been investigated much. Chaudier[12] made only a few observations

1 Maxwell, *Pogg. Ann.*, 1874, **151**, 151.
2 *Z. Phys. Chem.*, 1925, **118**, 1.
3 *Wied. Ann.*, 1881, **13**, 110.
4 *J. d. russ. Phys. Chem. Ges.*, 1905, T. **37**, 39.
5 *Diss. Upsala*, 1924, 139.
6 *Ann. Physik.*, 1904, (4) **15**, 28.
7 *Atti. Linc.*, 1910, (5) **19**, 470.
8 *Elster-Geital-Festschrift*, 1915, 453.
9 *Atti. Linc.*, 1926, (6) **3**, 28.
10 *Z. Phys. Chem.*, 1921, **98**, 293; 1923, **105**, 119.
11 *Ibid.*, 1924, **114**, 161.
12 *Compt. Rend.*, **137**, 248.

with some suspensions, but Diesselhorst, Freundlich and Leonardt[13] found that with the exception of vanadium pentoxide sol, no other colloidal solution exhibited this behaviour. Bergholm and Bjornstahl,[14] have, however, shown that the double refraction is also induced by an electric field in gold and silver sols.

Majorana[15] was the first to observe that a solution of "Fer Bravis" when subjected to a magnetic field exhibited birefringence and Schumass[16] suggested that the phenomenon is due to the orientation of colloidal particles. Cotton and Moutan[17] inferred on the basis of their extensive investigations that ferric oxide and other iron colloids consisted of ælotropic particles. Freundlich and collaborators[18] observed magnetic birefringence with vanadium pentoxide sols whilst Bjornstahl[19] found a positive magnetic birefringence with gold, silver, platinum, 10-chloro-phenanthrene-6-sulphonic acid and antimony sulphide sols, and negative birefringence with congo red, mechanically prepared sulphur sol and chlorophyll sols. Recently, Heller[20] has published a detailed account of his studies on ferric hydroxide sols.

The author is interested in the study of hydrophilic colloids from the view-point of jelly formation. Up till now, only a few hydrophilic colloids have been examined from this point of view. Many substances show in colloidal solution, a double refraction of the same sign as in the amorphous solid state. Umlauf[21] has found that the sols of cherry gum and tragacanth have positive and those of collodion, gelatine and gum arabic negative double refraction under high mechanical stress. Ambronn[22] found that the dry gel of cherry gum shows under tension and compression a double refraction like that of glass, but if the gel is allowed to swell in alcohol, then under a quick pressure it shows the double refraction of the same sign, but this gradually passes into one of a reversed sign.

In the present paper, some results on the mercuri-sulphosalicylic acid sols have been given with respect to the magnetic birefringence. This sol is known to give jellies under various conditions. Some other sols have

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13 *Elster-Geitel Festschrift*, 1915, 476.
14 *Phys. Zeit.*, 1920, **21**, 137.
15 *Atti. Linc.*, 1902, **11**, I, 374, 463, 531; II, 90, 139.
16 *Ann. Physik.*, 1903, (4) **10**, 658; **12**, 186.
17 *Ann. chim. et Physique*, 1907, (8) **11**, 145, 289.
18 *Loc. cit.*
19 *Phil. Mag.*, 1921, **42**, 352.
20 *Z. Physik. Chem.*, 1933, **166**, 365; *Kolloid-Beihefte*, 1933, **39**, 1.
21 *Wied. Ann.*, 1892, **45**, 544.
22 *Wied. Ann.*, 1889, **38**, 159.

also been examined. Besides the concentration effect of the sol and the influence of electrolytes, which the author has reported in one of his previous publications,[23] the influence of a number of peptising and sensitising substances has also been studied.

2. Experimental.

The experimental arrangement adopted for the present investigations was that described by Chinchalkar[24] for the study of solutions. A point-o-lite lamp of 1,000 c.p. was used as a source, the light from which condensed and collimated before passing through the polariser of which the principal direction of vibration was inclined at 45° to the horizontal. The sol to be investigated was placed in 33 cm. long tubes between the two poles of an electromagnet, the poles being 33 cm. wide. A long glass strip under pressure or strain was used as a compensator. The strip bent in its own plane would produce different layers above and below the neutral axis which will behave like a series of uniaxial positive and negative crystals with their axes parallel to the neutral axis. The beam of plane polarised light, after being allowed to pass through this compensator strip is examined with a crossed Nicol and a telescope atttached to an Adam-Hilger micrometer eyepiece. A current of about 2 to 3 amperes was passed throughout the electromagnet producing a field of 4,400 to 6,500 gauss. Nitrobenzene along with the same strained compensator was used as a standard for comparison, and the readings have been recorded in the terms of micrometer scale.

Influence of the field strength.—The field strength of the electromagnet was varied by changing the amount of current. 1·8% mercuri-sulphosalicylic acid sol was used. Mercuri-sulphosalicylic acid was prepared by dissolving freshly precipitated and well washed mercuric oxide in a concentrated solution of 5-sulphosalicylic acid, till a white gel was obtained. The gel was dried over water-bath and the white powder thus obtained was kept in well stoppered bottle, because the substance appears to absorb moisture from the atmosphere. A weighed amount of the substance was allowed to soak in distilled water for about 20 minutes and then shaken and diluted to the required volume. The sol thus obtained is almost clear with a few particles of suspension which are removed by filtration. It has been observed that the magnetic birefringent values markedly depend upon the mode of the preparation of the colloidal solution whereby the suspensions of different dispersity are obtained, and therefore, in one set of experiments, one and the same sol was used.

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[23] *J. Indian Chem. Soc.*, 1934, **11**, 449.
[24] *Indian J. Phys.*, 1931, **6**, 165.

TABLE I.

Field strength in Gauss	Micrometer readings with	
	Nitrobenzene	1·8% Colloid
4,200	34	34
5,300	75	51
7,400	102	67
21,000	Beyond scale	118

From these readings, it would be seen that the variation in the field strength produces comparatively less change in the colloid than in nitrobenzene.

Influence of ageing.—A 2% of the mercuri-sulphosalicylic acid sol was kept for a number of days and the values for the magnetic birefringence were determined from day to day. The relative birefringence is given in the following table with 100 as the value for nitrobenzene.

TABLE II.

Days	Relative birefringence
0	100
1	83·33
2	66·16
4	66
6	65·30

The freshly prepared sample of the colloidal suspension is more birefringent but the value markedly diminishes within the next two days, after which a constant is attained.

Influence of concentration.—Mercuri-sulphosalicylic acid sol of 2% concentration was prepared and then it was diluted to different concentrations and the relative values of magnetic birefringence were determined.

TABLE III.

Concentration in per cent.	Relative birefringence (nitrobenzene = 100)
2·0	92·6
1·0	58·4
0·5	25·9
0·4	18·1

These results show that the birefringence is roughly proportional to the concentration of the sol. During the first few dilutions, the anomaly is more marked.

The influence of electrolytes.—The influence of potassium chloride, potassium bromide, potassium nitrate and barium nitrate has been investigated in a foregoing publication.[25] Some of the results are summarised below. 10 c.c. of 2% sol were mixed with varying concentrations of electrolytes as given in the table and the total volume was made 20 c.c. by adding the

TABLE IV.

Amount of electrolyte added in c.c.	Relative birefringence with			
	N/10 KCl	N/35 KBr	N/20 KNO_3	0·5% $Ba(NO_3)_2$
0·0 ..	58·4	43·5	43·5	43·5
0·5 ..	40·6	38	..	..
1·0 ..	29·6	32·4	53·7	43·5
2·0 ..	..	44·3	65·7	44·4
3·0 ..	19·4	58·3	93·5	46·3
4·0 ..	..	..	122	..
5·0 ..	..	75·9	..	..
10·0 ..	..	162·0	..	..

[25] *Loc. cit.*

calculated amount of water. The sol used with KCl was slightly different with a little more relative birefringence.

These results are interesting from the point of view that chloride ions are known to dissolve out the colloidal phase as has been shown by Ostwald and Mertens,[26] and as the colloidal phase disappears, the non-spherical nature of the particles also tends to become isotropic, and the values for magnetic birefringence fall down. In presence of small traces of potassium bromide, a similar effect is observed. Perhaps at low concentrations, the sol gets more stabilised by the adsorption of negatively charged bromide ions and also the bigger aggregates disintegrate with the formation of less anisotropic particles. But at higher concentrations, the influence of the oppositely charged coagulating ions comes into the action, and the bigger aggregates formed in the process are more non-spherical. This goes to increase the values for magnetic birefringence. Nitrate ions are not markedly adsorbed from potassium nitrate solution, and the coagulating action begins even at low concentrations. Similar results are obtained with even very dilute barium nitrate solutions. With higher concentrations of this substance, the particles are so developed as to cause excessive scattering diminishing the intensity of the transmitted light and also bringing about the depolarisation. This is due to the bivalency of barium ions bringing about more effective coagulation.

Influence of sucrose.—10 c.c. of 2% mercuri-sulphosalicylic acid were mixed with different amounts of 20% sucrose solution and the total volume was made upto 20 c.c. in every case by mixing the required amount of water. 2 amperes current was used and the shifts on the micrometer scale for magnetic birefringence were recorded.

TABLE V.

System	Micrometer shifts	Relative birefringence
Nitrobenzene	39	100
10 c.c. sol + 10 c.c. water	18	46·15
10 c.c. sol + 1 c.c. sugar + 9 c.c. H_2O ..	15	38·46
10 c.c. sol + 2 c.c. sugar + 8 c.c. H_2O ..	12	30·77
10 c.c. sol + 3 c.c. sugar + 7 c.c. H_2O ..	16*	41·02*

* The colour dispersion.

[26] *Koll. Chem. Beih.*, 1926, **23**, 242.

The sugar is well known as an efficient peptiser of sols, and from the above results it will be seen that during the course of its action on the surface, it either disintegrates the anisotropic particles or in some other way makes them less non-shperical. The optical activity of sugar solutions causes difficulty in studying the influence of higher concentrations of this substance as a peptiser.

Influence of glycerol.—Experiments similar to those described above have been done with glycerol. Varying amounts of the substance have been added to 2% mercuri-sulphosalicylic acid sol, and the total volume was always made 20 c.c. The amount of sol taken was always 10 c.c. 2 amperes current was used.

TABLE VI.

System	Micrometer shifts	Relative birefringence
Nitrobenzene	130	100
10 c.c. sol + 10 c.c. water	61	47
10 c.c. sol + 4 c.c. glycerol + 6 c.c. H_2O	53	41
10 c.c. sol + 6 c.c. glycerol + 4 c.c. H_2O	28	21
10 c.c. sol + 10 c.c. glycerol ..	22	17

The presence of glycerol along with a colloidal suspension brings about the dehydration of the hydrated particles, and also causes peptisation by forming a layer at the surface of the particle and our values show that it disintegrates the particles to a much smaller size and the particles thus obtained are more spherical than the former particles in the absence of glycerol.

Influence of urea.—Similar experiments with urea are described below. Varying amounts of 10% urea solution were added to 10 c.c. of 2% mercuri-sulphosalicylic acid sol and the total volume was made 20 c.c. $2\frac{1}{2}$ amperes current was used.

TABLE VII.

System	Micrometer shifts	Relative birefringence
Nitrobenzene	50	100
10 c.c. sol + 10 c.c. H_2O	23	46
10 c.c. sol + 5 c.c. urea + 5 c.c. H_2O ..	23	46
10 c.c. sol + 10 c.c. urea	24	48

The influence of urea does not appear to be marked on the magnetic birefringence of the sol. Urea is generally a well-known sensitiser. It appears that perhaps the results will be more marked by taking larger amounts of urea and the values for birefringence would slightly increase in its presence of which a slight tendency appears in the above table.

Influence of ethyl alcohol.—10 c.c. of the mercuri-sulphosalicylic acid sol were mixed with different concentrations of ethyl alcohol and the total volume was made 20 c.c. by adding water to it. $2\frac{1}{2}$ amperes current was used.

TABLE VIII.

System	Micrometer shifts	Relative birefringence
Nitrobenzene	102	100
10 c.c. sol + 10 c.c. water	39·1	38·3
10 c.c. sol + 3 c.c. alcohol + 7 c.c. H_2O	39	38·3
10 c.c. sol + 5 c.c. alcohol + 5 c.c. H_2O	39	38·3
10 c.c. sol + 8 c.c. alcohol + 2 c.c. H_2O	37	36·2
10 c.c. sol + 10 c.c. alcohol	22	21·6

Small concentrations of alcohol appear to be without influence but the addition of a larger amount of alcohol beyond a certain limit causes at once a marked dehydration and disintegration of the colloidal particles with the result that the birefringent value falls down.

Influence of acetone.—The results exactly similar to those by alcohol have been obtained with acetone. To a 10% sol, varying amounts of acetone have been added, and the total volume was made upto 10 c.c. as before. $2\frac{1}{2}$ amperes current was used.

TABLE IX.

System	Micrometer shifts	Relative birefringence
Nitrobenzene	90	100
10 c.c. sol + 10 c.c. water	33	36·6
10 c.c. sol + 4 c.c. acetone + 6 c.c. water	34	37·7
10 c.c. sol + 6 c.c. acetone + 4 c.c. water	17	19
10 c.c. sol + 10 c.c. acetone .. .	0	0

The results are interesting from the point of view that the mercuri-sulphosalicylic acid sol can be rendered non-birefringent by adding sufficient amount of acetone.

Fresh mercuri-sulphosalicylic acid.—In all the above experiments, the mercuri-sulphosalicylic acid used was the one obtained by dissolving mercuric oxide in sulphosalicylic acid, and drying out the gel. This dried powder formed a reversible sol when again dispersed along with water, and the colloidal solution thus formed was found to be magnetically birefringent. It was interesting to see whether the non-dried freshly prepared colloidal solution was also birefringent. A 5% suspension of well washed mercuric oxide was prepared in water and it was mixed with a 50% solution of 5-sulphosalicylic acid. The magnetic birefringence of the sulphosalicylic acid and also this freshly formed colloidal solution was determined. $2\frac{1}{2}$ amperes current was used in the magnet to give a field of 5,200 gauss.

TABLE X.

System	Micrometer shifts
Nitrobenzene	83
5-sulphosalicylic acid, 50% solution	15
20 c.c. of acid + 8 c.c. of HgO suspension	15
20 c.c. of acid + 12 c.c. of HgO suspension	16·5
The above suspension after 2 hours	16

These results show, that mercuri-sulphosalicylic acid sol, freshly prepared does not exhibit more birefringence than the sulphosalicylic acid itself, which being an aromatic compound would certainly exhibit some birefringence. This is only the reversible dried gel which is so highly birefringent. In the course of time, it has been shown by the author, that a concentrated freshly prepared sol gives a jelly, but slight separation of the solid phase causes inconvenience in measuring the magnetic birefringence at different stages at various times.

The non-birefringent jelly-forming systems.—It has been sometimes led to believe the hydration tendency is associated with the non-spherical nature of particles, and perhaps these non-spherical particles help in the formation of chains so essential for a jelly structure by providing a number of corners. The vanadium pentoxide sol exhibits high magnetic birefringence and is

also known to give excellent jellies. Mercuri-sulphosalicylic acid and also some dyestuffs show magnetic birefringence and give jellies. The following jelly-forming systems were tried for magnetic birefringence:

(1) Thorium phosphate and thorium molybdate systems obtained by adding potassium phosphate or molybdate solutions to thorium nitrate solution as described in previous papers. The optically clear sols did not exhibit any marked magnetic birefringence even with a very high magnetic field.

(2) Ferric arsenate and ferric phosphate sols obtained by adding potassium arsenate or potassium phosphate to ferric chloride in excess and dialysing the sols so as to give jellies. These sols when diluted did not exhibit any marked birefringence.

(3) Lithium urate sol freshly prepared by adding lithium carbonate to uric acid suspended in water. No birefringence was observed. The sol precipitates out during the course of some time and just before this, its particles show orientation in the magnetic field.

3. Discussion.

The exhibition of magnetic double refraction by colloidal particles is due to their non-spherical nature, or in other words, their asymmetry. According to Langevin's theory, the magnetic and optical anisotropies are both combined to give this effect. What is true for the case of molecules may be also true for the colloidal electrolytes, colloidal micelles and even bigger aggregates of colloids. In a heterogeneous colloidal system, all these states may simultaneously exist in equilibrium:

Colloidal electrolytes of molecular dimensions $\rightleftarrows$ **Colloidal micelles of far ultra-microscopic dimensions** $\rightleftarrows$ **Colloidal aggregates visible under ultramicroscope**

As the ageing of a sol proceeds, the tendency of the system is to transform itself to the colloidal aggregate system. It is very likely that the colloids of molecular dimensions may be isotropic but as the system tends towards the formation of bigger colloidal aggregates, the anisotropy might markedly develop. The growth of an aggregate from a colloidal bath is not just the same as the growth of a crystal from a saturated system, and therefore, in many cases, anisotropic aggregates have been obtained from the suspensions containing isotropic particles. Only the very aged ferric hydroxide colloids are anisotropic. A freshly prepared sol does not exhibit magnetic birefringence. The fresh vanadium pentoxide sol is also non-birefringent. In the case of mercuri-sulphosalicylic acid sol also, as is seen from the results recorded in this paper, the freshly formed system by dissolving mercuric oxide in sulphosalicylic acid is not birefringent. It is only the reversible sol obtained

by dispersing the dried powder which exhibits the anisotropy to such an extent. From all these observations, it is clear that in most of these cases, the sols do not possess their intrinsic molecular anisotropy; it is only at some later stage that the isotropic particles assume rod or disc shapes and show rod or disc double refraction.

It appears to be very likely that the hydrophobic sols exhibit more anisotropy than the hydrated ones, as if the water layers around an asymmetric particle tend to smoothen the corners, and give more or less a symmetric spherical shape. Two sorts of hydration may be distinguished in this way: (i) Firstly, those hydrated viscous sols which show marked stream double refraction and also the electrical and magnetic birefringence,—these contain anisotropic particles of almost lyophobic nature, their hydration is essentially structural and not surficial, and they show mostly the structural viscosity. The structurally imbibed water is incapable of transforming the micellar anisotropy to a symmetrical spherical shape. (ii) Secondly, those lyophilic suspensions which do not show marked electric, stream or magnetic birefringence. In their case the surficially imbibed water layers have given rise to an isotropic spherical shape, they exhibit true viscosities. The water layers form the actual portion of the colloidal micelles.

The ageing effect on colloids may also be explained on this basis. It has been shown that ageing brings about the development of an anisotropic structure. This may be due to two reasons. In the case of hydrophilic substances, the surface energy decreases as the ageing proceeds, and some of the surficially adsorbed water is given out. This reverse process again makes the spherical particle a non-spherical one, and then on ageing, the system becomes more birefringent. In some cases, the agglomeration tendency of the particles also increases, and finer particles go to make bigger aggregates. In such cases also, it is likely that non-spherical particles may grow out from the spherical ones, as the aggregation phenomenon is not necessarily symmetrical. On account of these two reasons, we find that the hydrous ferric oxide and vanadium pentoxide sols show birefringence when they are aged.

Most of the jelly-forming sols, at least unless they are markedly aged, do not show birefringence. We also know that on ageing, the hydration tendency and hence the jelly-forming tendency gradually decreases. Thus, it appears that the non-spherical nature of particles cannot be associated with the jelly formation. In fact, when a water layer is allowed to envelop round a particle the surface forces are so symmetrical as to give a spherical covering. The anisotropic particle also thus becomes a spherical one.

In case of mercuri-sulphosalicylic acid, the sol has been obtained by a reverse way, and therefore, the aggregates are bigger in a freshly formed sol; and as the time proceeds, by the bombardment of the solvent over the solute, the aggregates become smaller and smaller, and during the course of disintegration they become less anisotropic also. This is why, the aged sol shows much less magnetic birefringence than the fresh one.

The influence of organic substances like sugar, glycerine, urea, alcohol and acetone throw some important light on the phenomenon of peptisation and sensitisation. In most of the cases, it has been found that the values for birefringence decrease. The peptising influence of organic substances may be due to the following reasons[27]: (i) The aggregation tendency of the paritcles markedly diminish in their presence as they form an envelop round the particles. (ii) By forming a double layer similar to Helmholtz double layer, the particles are protected from the action of oppositely charged ions. (iii) By actually changing the dielectric, they modify the electrical properties of the system to a marked extent. In some cases, it might also happen that the organic substances may bring about the disintegration of the colloidal aggregates. At least in the case of sensitisers, this effect is more likely to be marked. The disintegration may be either due to the actual bombardment of the organic solvent against the colloidal aggregates, or it may be spontaneous when the dielectric has been changed. In case of peptisers like glycerine or sugar, the decrease in the birefringence may be due to the formation of an isotropic layer of the substances round the particles. In the case of alcohol, acetone, etc., it may be due to both the reasons but mainly due to the disintegrations to smaller isotropic particles. A slight decrease in the value may be simply due to the change in dielectric constant of the dispersion medium, and the particles experience difficulty in orienting themselves in the electromagnetic field. In fact, in case of colloids, all these factors go to contribute something,—sometimes in the same direction and sometimes oppositely.

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Abstract.

The magnetic birefringence of mercuri-sulphosalicylic acid sol has been studied in detail. The fresh sol directly obtained by dissolving mercuric

[27] Prakash, *Z. anorg. Chem.*, 1931, **201**, 301.

oxide in sulphosalicylic acid is non-birefringent, but the reversible dried powder when dispersed in water gives birefringent sol. The birefringence increases as the magnetic field increases but not in the same proportion as in the case of nitrobenzene. The birefringence is also almost directly proportional to the concentration. In presence of dissolving ions, as chloride, the birefringence markedly diminishes, while in presence of nitrate ions or barium ions, it increases. The influence of peptisers and sensitisers as sugar, glycerine, ethyl alcohol, acetone and urea has also been investigated. With the exception of urea which does not produce any marked effect, in all other cases, the birefringence values decrease. With alcohol and acetone the fall is much marked. These results have been discussed and it has been shown that in their presence the anisotropy of the particles is decreased on account of disintegration of bigger aggregates to isotropic smaller ones and also due to the formation of spherical micelles by adsorbing layers of organic solutions round the originally anisotropic particles.

It has been shown that many of the well-known jelly-forming sols do not exhibit magnetic birefringence, and hence, it is not necessary to have non-spherical particles essential for jelly formation. On the contrary, it is also likely that the non-spherical lyophobic particles also become isotropic by becoming hydrated under favourable conditions.

THE RAMAN SPECTRA OF SULPHUR AND PHOSPHORUS.

Part I. Polarisation and Molecular Structure.

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1. Introduction.

SULPHUR and phosphorus are two common elements whose molecular structures have not been definitely determined till now. Sulphur, particularly, is interesting in view of the fact that it is known to possess certain properties which are apparently mutually contradictory in the light of the present-day knowledge regarding molecular phenomena. Thus, rhombic sulphur consisting of S_8 molecules[1] yields a large number of absorption bands in the infra-red[2,3] which suggests the existence of at least an induced electric moment between the neighbouring atoms in the molecule. This is contradicted by the fact that no electric moment[4] has been hitherto observed for this substance. The Raman spectrum[5] of crystals of rhombic sulphur yields four intense and three weak lines whose frequency shifts correspond fairly closely with those of the infra-red absorption bands. If we assume with Krishnamurti[5] that the four intense Raman lines in it are due to the symmetrical oscillations of S_{16}, S_8, S_4 and S_2 (a view which, however, requires modification) the presence of intense absorption at the corresponding wavelengths appears to be inexplicable. The homopolar nature of the sulphur molecule seems also to be fairly established since no detectable changes in frequency have been observed for the strong Raman lines due to a change from the solid to the liquid condition.[6] An attempt has been made in this communication to picture a molecular form for sulphur which could explain

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[1] Ephraim, *Anorganische Chemie*, Steinkopff, Dresden and Leipzig, 1934.

[2] Barnes, R. B., *Phys. Rev.*, 1932, **39**, 562.

[3] Taylor and Rideal, *Proc. Roy. Soc.*, A, 1927, **115**, 589.

[4] Rosenthal, S., *Zeit. Physik.*, 1930. **66**, 652 and 657; Dobinski, S., *Bull. Acad. Polonaise*, 1932, A, 239; Curtis, H. J., *J. Chem. Phys.*, 1933. **1**, 247.

[5] Krishnamurti, P., *Ind. Jour. Phys.*, 1930, **5**, 587; 105.

[6] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 120.

qualitatively some of these perplexing facts. It is well known that the polarisation characters of the Raman lines is a sure guide for the determination of the modes of oscillation of the molecule responsible for them. In the present paper the state of polarisation of the Raman lines of sulphur and phosphorus has been studied with particular reference to their molecular structure.

2. *Experimental Arrangements and Results.*

The chief handicap in the investigations on the light scattering in liquid sulphur and phosphorus is the difficulty for obtaining them in a fairly dust-free condition. Even freshly prepared crystals contain large quantities of dust particles which are hard to remove. The method of double-bulb distillation usually employed for ordinary liquids is inapplicable to these high-boiling-point substances due to a strong tendency in them for bumping. In the latter cases the following modification of vacuum distillation is found to work well. The experimental tube is attached to a long cylindrical tube containing the substance and connected to a vacuum pump through the usual drying columns. The distillation is performed either with the pump on or by sealing off the system after thorough evacuation. A small flame is played only *at the top portion of the substance* in the cylindrical tube, keeping the bottom layers comparatively at a low temperature and the liquid distils over slowly into the Raman tube.

During exposure, the substances are kept in a molten condition by placing a heating coil below the experimental tube and the temperature of the substance is maintained at the melting point either by adjusting the distance of the heater from the latter or by regulating the current in it. Direct exposure to the ultra-violet radiations of the mercury arc converts yellow phosphorus to red and deepens the colour of the molten sulphur; in the case of the solution of sulphur in carbon disulphide, colloidal sulphur is precipitated. These vitiating effects of the source are avoided by putting in the path of the incident light a Zeiss yellow glass-filter which transmits the green and the yellow radiations while cutting off the rays upto 4916 A.U. almost completely.

The horizontal and the vertical components of the scattered radiation are separated by means of a large quartz double-image prism and photographed simultaneously on the plate. The state of polarisation of the Raman lines is determined as detailed in a previous paper[7] after making due allowance for errors of experimentation.

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[7] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, **4**, 174.

The results of the investigation are given in Tables I and II and enlarged photographs of the spectra of the two elements are reproduced in the accompanying plates.

TABLE I.

Sulphur.

No.	Infra-red frequency in cm.$^{-1}$ (Barnes)	Raman frequencies in cm.$^{-1}$						
		Rhombic 25°C.		Mono-clinic 110°C.	Liquid 115°		Solution in CS_2 50%	
		Krishna-murti	Author		Author	ρ	Author	ρ
1	< 77	..	..					
2	87(w)	85(m)	88(5)	80(0)	80(2,d)	D	Wing of CS_2	D
3	103(w)	..	114(0)	..	..			
4	150(st)	152(st)	152(10)	152(5)	152(10)	D	152(10)	$\lesssim$0·82
5	200—250(st)	183(w)	185(0, d)	..	185(0, d)	..		
6	..	216(st)	216(10)	216(5)	216(10)	P	216(10)	0·23
7	..	243(w)	243(1, d)	..	243(1, d)	..	..	
8	267(w)	..	..	..				
9	400(w)	434(w)	434(2, d)	..	434(3d)	D	434(2)	D
10	465(st)	470(st)	468(10)	470(5)	470(10)	P	470(10)	0·08
							655(st) CS_2	0·19

st = strong, w = weak, m = medium intensity, d = diffuse.

TABLE II.

Liquid Phosphorus.

Raman frequencies.

No.	$\Delta\nu$ in cm.$^{-1}$	Intensity	ρ
1	606	10	0·05
2	465	6	$\lesssim$ 0·87
3	363	2	$\lesssim$ 0·85

N.B.—D means the depolarisation ratio ρ is equal to or greater than 6/7 and P means that $\rho < 6/7$.

3. Discussion of Results.

(*a*) *In relation to the molecular structure of Phosphorus.*—According to chemical evidence yellow phosphorus consists of P_4 molecules both in the solid and liquid state. A complete analysis of the crystal structure of yellow phosphorus has not yet been made due probably to the fact that X-rays transform white to the red form.[8] Natta and Passerini,[9] however, announced that by cooling the sample to $-35°$ C., they succeeded in obtaining 22 lines of a cubic pattern. It may, therefore, be reasonable to assume that crystalline yellow phosphorus has a molecular cubic lattice formed of P_4 molecules. The four atoms in the molecule can occupy either the corners of a square or form a regular tetrahedron. Bhagavantam[10] was the first to show that in the Raman effect the former would give four lines while in the latter only three would appear. His investigation[11] yielded only three lines in support of a tetrahedral structure for the P_4 molecule. The recent measurements of electron diffraction[12] by phosphorus vapour also rule out the square model and confirm the structure proposed by Bhagavantam. From the identity of the Raman spectra of phosphorus in different states[13] it is to be concluded that the molecular form remains unchanged upto 450° C.

It was not, however, possible to obtain a good spectrogram for phosphorus in the previous work due to the rapid conversion of the yellow to the opaque red variety. In the present investigation, an intense spectrum has been obtained for the distilled liquid and the carefully cooled solid, where the faint line at 360 which was reported as doubtful in the earlier paper has come out with medium intensity. Except one near the Rayleigh line whose origin will be discussed in the second part, no other line has appeared in the spectrum, which is the result to be expected from the dynamics of the tetrahedral molecule.

The strong and sharp line at 606 is highly polarised and therefore, belongs to the breathing frequency of the tetrahedron. The lines at 465 and 363 are both diffuse and depolarised to an extent of 6/7 in accordance with the fact that they owe their origin to the two degenerate vibrations. Microphotometric measurements of intensities of the lines are in the ratio 10 : 6 : 2. The valence force f, between P — P as calculated from the relation $\omega = 2\pi\sqrt{\frac{4f}{m}}$ is $1{\cdot}64 \times 10^5$ dynes per cm.

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[8] Jung, *Centralblatt. f. Min. u. Geol.*, 1926, 107–114.
[9] Natta and Passerini, *Nature*, 1930, **125**, 707.
[10] Bhagavantam, S., *Ind. Jour. Phys.*, 1930, **5**, 73.
[11] Bhagavantam, S., *Ibid.*, 1930, **5**, 35.
[12] Maxwell, Hendricks and Mosley, *Jour. Chem. Phys.*, 1935, **3**, 699.
[13] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 260.

(*b*) *In relation to the molecular structure of Sulphur.*—From the X-ray studies of rhombic sulphur Mark and Wigner[14] concluded that the unit cell contains 128 atoms grouped as eight molecules of 16 atoms each. To explain the strong infra-red absorption observed for sulphur, Taylor and Rideal[15] assumed this structure to be correct and postulated that the S_{16} molecule consists of 8 (S_2) groups which are situated at the corners of a cube. They further believed that the S atoms forming the S_2 groups possess a pseudo-hetropolar binding and have an induced electric moment equivalent to 0·7 times the electric moment it would have if one electron had actually been transferred from one sulphur atom to the other. But recently the structure of rhombic sulphur has been re-determined by Warren and Burwell[16] and they have concluded that it belongs to the Space group V_h^{24} (Fddd) with sixteen S_8 molecules in the unit cell. They have pointed out that each molecule containing 8 atoms of sulphur assumes a symmetrical puckered ring which is made up of two squares one turned 45° with respect to the other (Fig. 1). The planes of the two squares are separated by 1·15 A.U.,

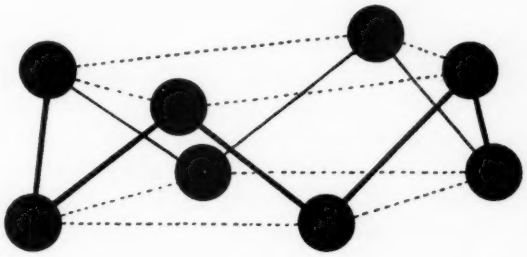


FIG. 1.

Sulphur Molecule. Unbroken lines indicate co-valent bonds and the dotted lines co-ordination bonds.

the side of the square is 3·38 A.U. and the valence angle is 105°. This structure has found good support from the measurements of magnetic susceptibility* along the three axes of the crystals of rhombic sulphur.

The structure given by Warren and Burwell, however, does not explain the strong infra-red absorptions of sulphur which depend only on the change in the electric moment during the vibrations of the molecule. For this purpose, we assume that the neighbouring atoms in the plane of each

[14] Mark and Wigner, *Zeit. Phys. Chem.*, 1924, **111**, 398.

[15] Taylor and Rideal, *loc. cit.*

[16] Warren, B. E., and Burwell, J. T., *Jour. Chem. Phys.*, 1935, **3**, 6.

* Unpublished work of Mr. P. Nilakantan of this laboratory.

square are co-ordinately linked and hence they possess virtually opposite charges which in absorption act as electric dipoles (Fig. 2). This assumption

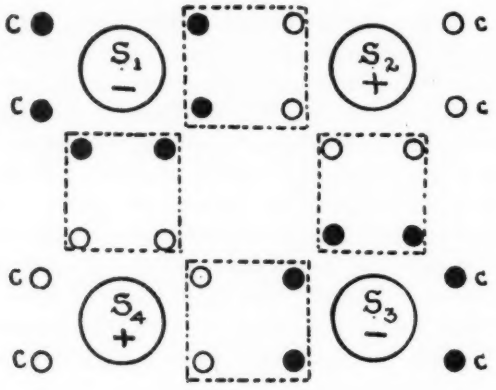


FIG. 2.

The electrons within the dotted square are linked with co-ordination bonds.

is justified for the following reasons. If we consider the four sulphur atoms S_1, S_2, S_3 and S_4 in the plane of one of the squares, each atom has six electrons in the outer shells of which two marked *c* are shared co-valently with two atoms in the other square. In the absence of any other bond, the octet of each of the eight atoms in the molecule is completed and the sulphur is di-valent. But we know that in the case of sulphur, the outer shell can expand to ten electrons as in sulphur tetrachloride and twelve electrons as in sulphur hexafluoride. In fact, Bassett and Durrant[17] assume that the chromogenetic properties of sulphur are to be attributed to the S atoms possessing a ten-electron sheath. Therefore, the two pairs of unshared electrons of the atoms S_1 and S_3 (Fig. 2) are co-ordinated with those of the neighbouring atoms S_2 and S_4 with the result that S_1 and S_3 possess twelve and S_2 and S_4 possess only eight electrons in their outer shells. This is equivalent to attributing a positive charge to S_2 and S_4 and a negative charge to S_1 and S_3 and the atoms become quadrivalent. The same is true of the units of the other square. From the geometry of the molecule it follows that no permanent electric moment could be discovered for the element.

Now we shall examine how far the Raman and the infra-red measurements lend support to the above molecular structure. A molecule with 8 atoms as in sulphur has eighteen normal vibrations out of which by reason

[17] Bassett, H., and Durrant, R. G., *J. C. S.*, 1927, 1401.

of symmetry some may be forbidden in the Raman effect and some may be degenerate. In rhombic sulphur eight Raman lines have been recorded including a new line at 114 which coincides with the infra-red absorption at 103. Three of these are very intense, one is of medium intensity and the rest are weak and diffuse. The line at 88 alone suffers characteristic changes in frequency, intensity and sharpness in passing to the liquid state.

Of the three intense lines the one at 470 is almost completely polarised and the line at 216 possesses a low depolarisation ratio. These two, therefore, belong to the totally symmetrical oscillations of the molecule. From Fig. 1 it is clear that the two possible symmetrical vibrations are (1) that in which the two squares are vibrating against each other, (2) that in which the four atoms in each square move towards or away from the centre of the square. The first mode of oscillation taking place in a direction parallel to the symmetry axis involves no change in the electric moment and should therefore be inactive in the infra-red. The second mode of oscillation which is perpendicular to the axis introduces changes in the electric moment due to the change in the distance between the units of the dipole as contemplated by co-ordination and therefore would give rise to absorption in the infra-red. The infra-red measurements, however, show that there is a marked absorption at points corresponding to both these frequencies ; but while the absorption is pretty sharp at about 470, it is extended over 50 wave-numbers at 216. As Barnes[18] himself remarks this latter region if explored by a finer grating would undoubtedly reveal finer structures. In the Raman effect, this line is accompanied on both sides by two faint and diffuse lines at 183 and 243. Due to their extreme weakness the state of polarisation of these lines could not be determined. It is only reasonable to assume that the strong absorption is due to anti-symmetric oscillations giving rise to these faint lines and does not have the same origin as the strong, sharp and well-polarised line at 216. Thus the line at 216 is to be attributed to the oscillations of the squares against each other. Wagstaff[19] calculates the atomic frequency of sulphur according to Einstein's formula $\nu = 2{\cdot}54 \times 10^7 \frac{V^{1/6}}{k^{1/2}M^{1/2}}$ where k = compressibility, V = atomic volume and M = atomic weight and gets a value $7{\cdot}3 \times 10^{12}$ vibrations per second, which in wave-numbers gives 243. If we consider the oscillations of the squares against each other as akin to an atomic vibration, the proximity of the observed frequency 216 to the calculated value 243 lends further support to the above assignment.

[18] Barnes, *Loc. cit.*

[19] Wagstaff, J. E. P., *Phil. Mag.*, 1924, **47**, 84.

The intense, sharp and polarised line at 470 is consequently to be attributed to the expansions and contractions of the squares constituting the molecule. As a first approximation, neglecting for a moment the influence of the atoms of one square over those of the other, the frequency corresponding to this oscillation is given by $\omega = \frac{1}{2\pi}\sqrt{\frac{2f}{m}}$.[20] If we further assume that the force between the neighbouring atoms along the side of the square is very nearly the same as for phosphorus, namely about $1 \cdot 75 \times 10^5$ dynes per cm., the calculated frequency comes to about 485. Involving as it does, great approximations and assumptions, the agreement between the calculated and the observed values justifies, to some extent, the assignment of the line to the expansions and contractions of the square.

The third line at 150 is depolarised to an extent of 6/7 and is presumably to be attributed to the torsional oscillations of the two squares against each other. The strong infra-red absorption observed at 150 evidently owes its origin to the same mode of oscillations of the molecule. The marked intensity and sharpness of a completely depolarised vibration is, however, surprising. The weak line at 434 is also completely depolarised and cannot therefore be considered as the overtone of 216. This line as well as the absorption at 400 is probably due to one of the anti-symmetric degenerate vibrations of the atoms in each square. The origin of the depolarised line at 88 will be discussed in the next paper.

It will be interesting to see how far the molecular structure proposed above could explain the physical properties of sulphur. It is well known[21] that when sulphur is heated it melts at 115° C. to form a brownish yellow transparent mobile liquid and as the temperature rises to about 220° C. it becomes more and more viscid and dark reddish brown in colour. At temperatures higher than 250° C. it attains a greater transparency and fluidity. On quenching the viscid liquid between 220°—250° C. in cold water a soft plastic product is obtained which after distension to four times its length regains its original form. If the liquid above 400° C. is poured in a thin stream into liquid air, it can be obtained as a fine thread of diameter 0·5–1 mm. This has an extraordinary elasticity at room temperature extending to 5·5 times its original length without passing its elastic limits. This elasticity is lost in half an hour.

On the basis of the structure proposed here, the presence of the co-ordinate bond between the neighbouring atoms in the plane of the square may

[20] Bhagavantam, S., *Ind. Jour. Phys.*, 1930, **5**, 73.

[21] Mellor, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, **10**, 43.

be considered as a barrier for the interpenetration of the molecules upto the melting point. As the temperature is raised, this bond of co-ordination which is weak, gradually gives way and the molecules are free to approach nearer as shown in Fig. 3. This transition may be assumed to take place

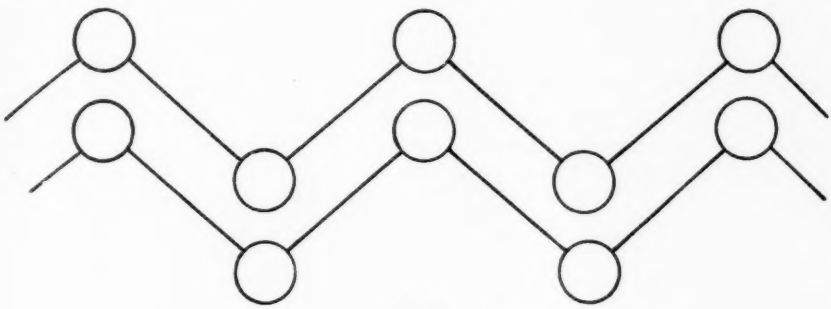


FIG. 3.

Showing the closer approach of two neighbouring molecules.

at about 160° C. which is the transition point at which the increase of viscosity begins. The process is to be considered as equivalent to polymerisation and accounts satisfactorily for the darkening of the colour and it is, therefore, unnecessary to postulate the formation of thiozone S_3 as has been proposed by Erdmann.[22] Any sudden cooling of the liquid at this stage gives a temporary setting to the interlocked puckered rings which would, as is to be expected, possess the great elasticity that has been observed in plastic sulphur. At temperatures near the boiling point of sulphur, the ring itself may break open and the staggered chains thus formed are capable of yielding the fine highly-elastic strings by sudden cooling to the temperature of liquid air. Finally, on boiling, the chain can be expected to break up further giving rise to double-bonded S = S molecules.

In conclusion the author desires to express his heartfelt thanks to Prof. Sir C. V. Raman for his inspiring interest in the work.

Summary.

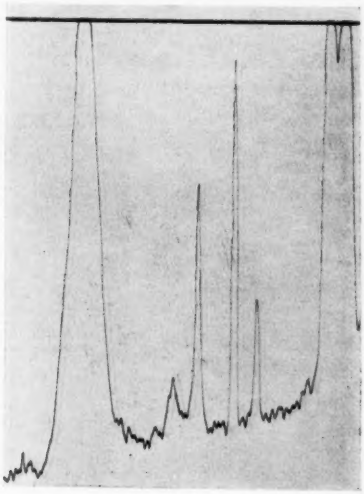
The polarisation of Raman lines of sulphur and phosphorus is investigated with reference to their molecular structures. An intense Raman spectrum of liquid phosphorus has yielded three lines the state of polarisation of which conforms to the Raman-active vibrations of a tetrahedral molecule. The molecule of sulphur is considered to be a symmetrical puckered ring made up of two squares of four atoms each, one square placed at 45° with

[22] Erdmann, H., *Liebig's Ann.*, 1908, **362**, 133.

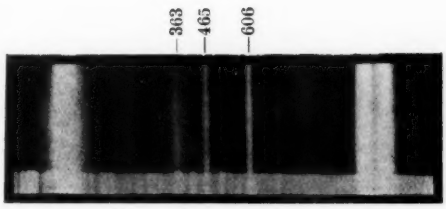
respect to the other. To explain the strong infra-red absorptions, the neighbouring atoms in the plane of each square are assumed to be connected with co-ordination bonds which give rise to electric dipoles causing absorption. The two lines 470 and 216 which are well-polarised are assigned to two symmetrical oscillations of such a model, 470 to the vibration in which the four atoms in each square move towards or away from the centre of the square and 216 to the vibration in which the two squares move towards or away from each other. The lines at 150 and 434 are completely depolarised and belong to anti-symmetric vibrations. The well-known changes of sulphur on heating are explained on the basis of this new molecular structure. A method of distilling high-boiling-point substances is also described in the paper.

(1)

Phosphorus Solid.

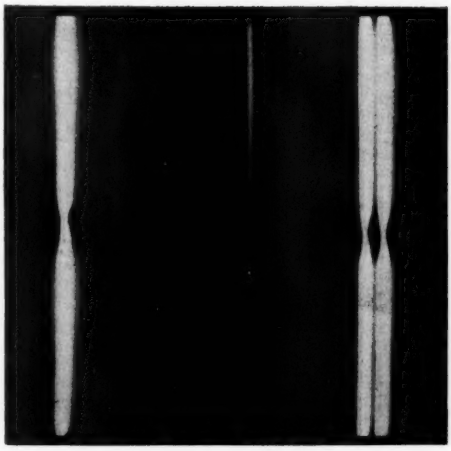


(2)

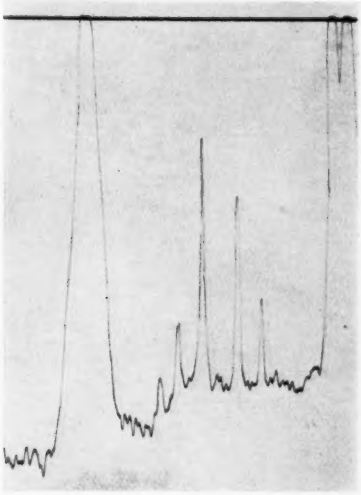


Phosphorus Liquid.

(3)



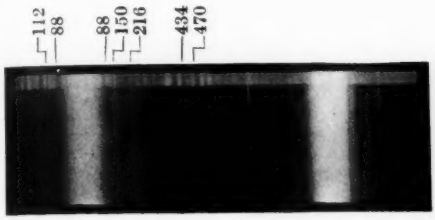
Phosphorus—Polarisation.



Microphotometric Curves of Fig. (3).

Top Vertical. *Bot.* Horizontal.

Raman Spectra.

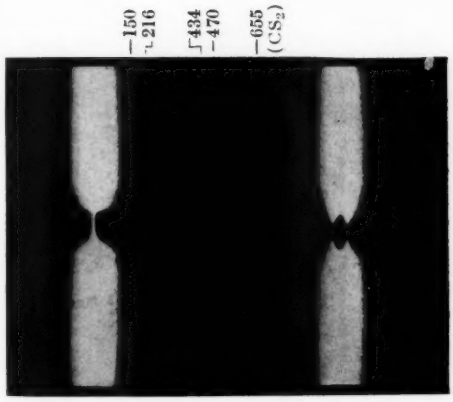


(1)

Rhombic Sulphur.

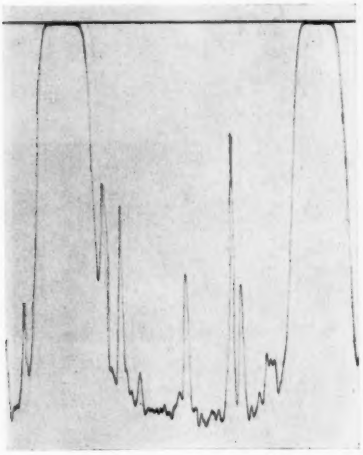
(2)

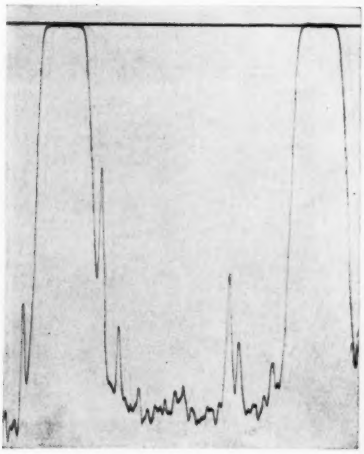
Liquid Sulphur.



(3)

Sulphur in CS_2—Polarisation.





Microphotometric Curves of Fig. (3).

Top Vertical. *Bot* Horizontal.

Raman Spectra.

RING-SINGULARITY IN BORN'S UNITARY THEORY—I.

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(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received August 17, 1936.

1. Introduction.

In two papers on the unitary theory of field and matter Born[1] has given a classical treatment of the derivation of the equations of motion of a point-singularity representing a particle. The chief assumption made is that the external field must be constant over the " diameter " of the particle. The method is to start from a variation principle representing both the motion of the field and the singularity, the latter part also being written as a space-time integral involving Dirac's δ-function. In addition Born has also introduced a spin for the particle and given a derivation of Kramers'[2] formulæ on the basis of the unitary theory. A treatment on similar lines without however introducing the spin has also been given by Pryce[3] who starts with the Hamiltonian instead of the Lagrangian.

In the second of the papers referred to above, Born has shown that the results obtained by Kramers are difficult to interpret on the basis of the unitary theory and shown that the difficulty disappears if the particle be assumed to have, besides the magnetic moment, a charge or an electric moment or both. This enables the derivation of a set of equations of motion which are a generalisation of Kramers' equations, self-consistent without imposing a restriction on the Lagrangian and satisfactory from the purely formal standpoint. Since, however, the elementary particles occurring in nature have no electric rest-moment the conclusion was drawn that, on the basis of the unitary theory, point-singularities were not the correct representation of the particles. It was finally suggested that there might be other possibilities.

I have considered in this paper an elementary particle as a ring-singularity. The principal results obtained can be summarised as under :—

(*a*) Finite expressions are obtained for the total energy and angular momentum.

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[1] M. Born, *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 8; *ibid.*, 1936, A, **3**, 85.

[2] H. A. Kramers, *Physica*, 1934, **1**, 825; Zeeman, *Verhandelingen*, 1935, p. 403.

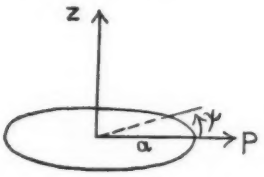
[3] M. H. L. Pryce, *Proc. Roy. Soc.*, A, 1936, **155**, 597.

(*b*) The ratio of the magnetic moment to angular momentum is obtained as $e/2\mu$ and not e/μ (μ = rest-energy) showing that we do not obtain an explanation of the spin.

(*c*) Taking the ring-singularity as representing a proton we can derive an estimate of the ring-radius so as to explain the high mass of the proton.

2. *Field Equations.*

Let the axis of symmetry be taken as the z-axis and the radius of the ring a. We introduce cylindrical co-ordinates ρ, ψ, z and assume axial symmetry. The linear density is given by $\eta = e/2\pi a$ and $\vec{v}$ denotes the velocity vector. We introduce the Dirac δ-function such that $\delta = \infty$ on the ring and



$$\int \delta d\rho dz = 1.$$

Proceeding as in the papers of Born quoted above[4] without using spin considerations we obtain the field equations for the stationary case in the form.

$$(2,1) \qquad \begin{cases} \text{rot } \vec{H} = \eta \vec{v} \delta\,; & \text{div } \vec{D} = \eta\delta\,; \\ \text{div } \vec{B} = 0\,; & \text{rot } \vec{E} = 0. \end{cases}$$

We shall now obtain the equations of transformation for vector-components in the case of axial symmetry and also derive expressions for the operators *div*, and *rot*.[5] From the equations of transformation,

$$\left.\begin{aligned} x &= \rho\cos\psi \\ y &= \rho\sin\psi \\ z &= z \end{aligned}\right\} \tan\psi = \frac{y}{x},\ \frac{\partial\psi}{\partial x} = -y/\rho^2 \text{ and } \frac{\partial\psi}{\partial y} = \frac{x}{\rho^2}$$

one has

$$\left.\begin{aligned} \frac{\partial}{\partial x} &= \frac{x}{\rho}\frac{\partial}{\partial\rho} - \frac{y}{\rho^2}\frac{\partial}{\partial\psi} \\ \frac{\partial}{\partial y} &= \frac{y}{\rho}\frac{\partial}{\partial\rho} + \frac{x}{\rho^2}\frac{\partial}{\partial\psi} \end{aligned}\right\} \text{ and } \frac{\partial}{\partial\rho}\frac{x}{\rho} = 0,\ \frac{\partial}{\partial\rho}\frac{y}{\rho} = 0$$

and therefore for any scalar ϕ of cylindrical symmetry $\left(\dfrac{\partial\phi}{\partial\psi} = 0\right)$

$$(2,2) \qquad \frac{\partial\phi}{\partial x} = \frac{x}{\rho}\frac{\partial\phi}{\partial\rho};\ \frac{\partial\phi}{\partial y} = \frac{y}{\rho}\frac{\partial\phi}{\partial\rho}$$

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[4] See Born, I, p. 10, equations (1, 9).

[5] I have to thank Dr. Beth, one of Prof. Born's pupils, for having communicated to me the correct proofs of the derivation of these expressions and of (2, 6).

and for any vector $\vec{A}$,

$$(2,3)\qquad \left\{\begin{array}{l|l} A_x = \frac{x}{\rho}A_\rho - \frac{y}{\rho}A_\psi & A_\rho = \frac{x}{\rho}A_x + \frac{y}{\rho}A_y \\ A_y = \frac{y}{\rho}A_\rho + \frac{x}{\rho}A_\psi & A_\psi = -\frac{y}{\rho}A_x + \frac{x}{\rho}A_y \end{array}\right.$$

Accordingly

$$\left.\begin{array}{l} \text{grad}_\rho\ \phi = \frac{\partial\phi}{\partial\rho} \\ \text{grad}_\psi\ \phi = 0 \\ \text{grad}_z\ \phi = \frac{\partial\phi}{\partial z} \end{array}\right\}$$

so that if a vector be a gradient it has no ψ-component.

To calculate div $\vec{A}$ for any arbitrary vector $\vec{A}$, we divide the vector field into two fields: $\vec{A} = \vec{B} + \vec{C}$, such that $B_\psi \equiv 0$, $C_\rho \equiv 0$, $C_z \equiv 0$, *i.e.*, $|C| = C = C_\psi$. We can prove that div $\vec{C} = 0$, for

$$\text{div}\,\vec{C} = \frac{\partial C_x}{\partial x} + \frac{\partial C_y}{\partial y} + \frac{\partial C_z}{\partial z} = \frac{\partial C_x}{\partial x} + \frac{\partial C_y}{\partial y}$$

$$\frac{\partial C_x}{\partial x} = \frac{\partial}{\partial x}\left[-\frac{y}{\rho}C\right] = -\frac{x}{\rho}\frac{\partial}{\partial\rho}\left(\frac{y}{\rho}C\right) + \frac{y}{\rho^2}\frac{\partial}{\partial\psi}\left(\frac{y}{\rho}C\right)$$

$$= -\frac{xy}{\rho^2}\frac{\partial C}{\partial\rho} + \frac{y}{\rho^2}C\,\frac{\partial}{\partial\psi}\frac{y}{\rho}$$

$$= -\frac{xy}{\rho^2} + \frac{xy}{\rho^3}C.$$

$$\frac{\partial C_y}{\partial y} = \frac{\partial}{\partial y}\left[\frac{x}{\rho}C\right] = \frac{y}{\rho}\frac{\partial}{\partial\rho}\left(\frac{x}{\rho}C\right) + \frac{x}{\rho^2}\frac{\partial}{\partial\psi}\left(\frac{x}{\rho}C\right)$$

$$= \frac{xy}{\rho^2}\frac{\partial C}{\partial\rho} - \frac{xy}{\rho^3}C$$

$$\therefore\ \frac{\partial C_x}{\partial x} + \frac{\partial C_y}{\partial y} = 0,\ \textit{i.e.},\ \text{div}\,\vec{C} = 0 \text{ and div } \vec{A} = \text{div } \vec{B};$$

$$\text{but, div}\,\vec{B} = \frac{\partial B_x}{\partial x} + \frac{\partial B_y}{\partial y} + \frac{\partial B_z}{\partial z}$$

$$= \frac{\partial}{\partial x}\left(\frac{x}{\rho}B_\rho\right) + \frac{\partial}{\partial y}\left(\frac{y}{\rho}B_\rho\right) + \frac{\partial B_z}{\partial z}, \text{ using (2, 3) since } B_\psi = 0$$

$$= \frac{B_\rho}{\rho} + x\frac{\partial}{\partial x}\left(\frac{B_\rho}{\rho}\right) + \frac{B_\rho}{\rho} + y\frac{\partial}{\partial y}\left(\frac{B_\rho}{\rho}\right) + \frac{\partial B_z}{\partial z}$$

$$= \frac{2B_\rho}{\rho} + x\frac{\partial}{\partial\rho}\left(\frac{B_\rho}{\rho}\right)\frac{\partial\rho}{\partial x} + y\frac{\partial}{\partial\rho}\left(\frac{B_\rho}{\rho}\right)\frac{\partial\rho}{\partial y} + \frac{\partial B_z}{\partial z}$$

$$= \frac{2B_\rho}{\rho} + \rho \frac{\partial}{\partial \rho}\left(\frac{B_\rho}{\rho}\right) + \frac{\partial B_z}{\partial z} \left[\text{since from } \rho^2 = x^2 + y^2 \right.$$

$$\left. x \frac{\partial \rho}{\partial x} + y \frac{\partial \rho}{\partial y} = \rho\right]$$

$$= \frac{B_\rho}{\rho} + \frac{\partial B_\rho}{\partial \rho} + \frac{\partial B_z}{\partial z}$$

Hence, for any arbitrary vector $\vec{A}$

$$(2, 4) \qquad \text{div } \vec{A} = \frac{1}{\rho}\left\{\frac{\partial(\rho A_\rho)}{\partial \rho} + \frac{\partial(\rho A_z)}{\partial z}\right\}.$$

We shall now calculate rot $\vec{A}$ for an arbitrary vector $\vec{A}$ which is however axially-symmetric, *i.e.*, for which

$$\frac{\partial A_\rho}{\partial \psi} = \frac{\partial A_\psi}{\partial \psi} = \frac{\partial A_z}{\partial \psi} = 0.$$

$$\text{rot}_x \vec{A} = \frac{\partial A_x}{\partial y} - \frac{\partial A_y}{\partial z} = \frac{y}{\rho}\frac{\partial A_z}{\partial \rho} - \frac{y}{\rho}\frac{\partial A_\rho}{\partial z} - \frac{x}{\rho}\frac{\partial A_\psi}{\partial z}$$

$$\text{rot}_y \vec{A} = \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} = \frac{x}{\rho}\frac{\partial A_\rho}{\partial z} - \frac{y}{\rho}\frac{\partial A_\psi}{\partial z} - \frac{x}{\rho}\frac{\partial A_z}{\partial \rho}$$

$$\text{rot}_z \vec{A} = \frac{x}{\rho}\frac{\partial}{\partial \rho}\left\{\frac{y}{\rho}A_\rho + \frac{x}{\rho}A_\psi\right\} - \frac{y}{\rho^2}\frac{\partial}{\partial \psi}\left\{\frac{y}{\rho}A_\rho + \frac{x}{\rho}A_\psi\right\}$$

$$- \frac{y}{\rho}\frac{\partial}{\partial \rho}\left\{\frac{x}{\rho}A_\rho - \frac{y}{\rho}A_\psi\right\} - \frac{x}{\rho^2}\frac{\partial}{\partial \psi}\left\{\frac{x}{\rho}A_\rho - \frac{y}{\rho}A_\psi\right\}$$

$$= \frac{\partial A_\psi}{\partial \rho} + \frac{1}{\rho}A_\psi.$$

Hence,

$$(2, 5) \qquad \begin{cases} \text{rot}_\rho \vec{A} = -\dfrac{\partial A_\psi}{\partial z} \\ \text{rot}_\psi \vec{A} = \dfrac{\partial A_\rho}{\partial z} - \dfrac{\partial A_z}{\partial \rho} \\ \text{rot}_z \vec{A} = \dfrac{1}{\rho}\dfrac{\partial}{\partial \rho}(\rho A_\psi) \end{cases}$$

We shall now prove that for the field vectors $\vec{E}$, $\vec{H}$, $\vec{B}$, $\vec{D}$ satisfying the differential equations (2, 1), we have the relations

$$(2, 6) \qquad E_\psi = 0, \quad H_\psi = 0, \quad B_\psi = 0, \quad D_\psi = 0.$$

As regards $\vec{E}$, (2, 1) shows that it is irrotational and has no singularities. Hence it is the gradient of a non-singular scalar and from the theorem proved on p. 357, it follows that $E_\psi = 0$.

Next considering $\vec{H}$, we observe that it has a singularity and cannot be expressed as the gradient of an analytic scalar function. We write

$$\vec{H} = \vec{H}_{cl} + \vec{H}^1, \text{ the first term being the classical part}$$

on account of rot $\vec{H} = 0$ and rot $\vec{H}_{cl} = 0$, we get rot $\vec{H}^1 = 0$. Also $\vec{H}_{cl}$ has the same singularities as $\vec{H}$ and accordingly $\vec{H}^1$ has no singularities. This fact along with rot $\vec{H}^1 = 0$ enables us to deduce as above that $\vec{H}^1$ has no ψ-component. But $\vec{H}_{cl}$ is well-known and has no ψ-component. Accordingly $H_\psi = 0$.

The proof for $\vec{B}$ is obtained by considering

$$\vec{H} = \frac{\partial L_r}{\partial \vec{B}} \text{ where } L_r = L_r(F, G) \text{ is the Lagrangian}$$

$$i.e., \quad \vec{H} = L_{r_F} \frac{\partial F}{\partial \vec{B}} + L_{r_G} \frac{\partial G}{\partial \vec{B}} = L_{r_F} \vec{B} + L_{r_G} \vec{E}$$

Neither $\vec{H}$ nor $\vec{E}$ has a ψ-component. Hence at all places where $L_{r_F} \neq 0$, $\vec{B}$ also has no ψ-component.

A similar proof for $\vec{D}$ is obtained from

$$\vec{D} = -\frac{\partial L_r}{\partial \vec{E}} = -L_{r_F} \frac{\partial F}{\partial \vec{E}} - L_{r_G} \frac{\partial G}{\partial \vec{E}} = L_{r_F} \vec{E} - L_{r_G} \vec{B}$$

$\vec{E}$ has no ψ-component and $\vec{B}$ none when $L_{r_F} \neq 0$. Hence $\vec{D}$ has no ψ-component at all places where $L_{r_F} \neq 0$ or $L_{r_G} = 0$.

Using (2, 4), (2, 5) and (2, 6) we can now write the field equation (2, 1) in the form

$$(2, 7) \qquad \begin{cases} \dfrac{\partial H_\rho}{\partial z} - \dfrac{\partial H_z}{\partial \rho} = \eta v \delta\,; \dfrac{1}{\rho}\left\{\dfrac{\partial(\rho D_\rho)}{\partial \rho} + \dfrac{\partial(\rho D_z)}{\partial z}\right\} = \eta\delta \\ \dfrac{\partial(\rho B_\rho)}{\partial \rho} + \dfrac{\partial(\rho B_z)}{\partial z} = 0, \dfrac{\partial E_z}{\partial \rho} - \dfrac{\partial E_\rho}{\partial z} = 0 \end{cases}$$

since, further, in the stationary case $v_\rho = v_z = 0$, $v_\psi = v$. The Lagrangian is given by

$$(2, 8) \quad L_r = b^2 \left\{ \sqrt{1 + \frac{1}{b^2}(B_\rho^2 + B_z^2 - E_\rho^2 - E_z^2) - \frac{1}{b^4}(B_\rho E_\rho + B_z E_z)^2} - 1 \right\}$$

3. Boundary conditions at $\rho = a$.

Integrating the field equations over the element of volume

$$\int\int \frac{1}{\rho}\left\{\frac{\partial(\rho D_\rho)}{\partial \rho} + \frac{\partial(\rho D_z)}{\partial z}\right\} 2\pi\rho d\rho dz = \int\int \eta\delta \cdot 2\pi\rho d\rho dz = 2\pi a\eta = e$$

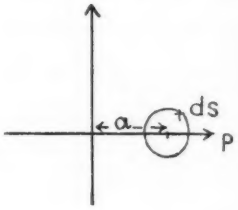
and the left-hand side

$$= 2\pi \int\int \left\{ \frac{\partial(\rho D_\rho)}{\partial \rho} + \frac{\partial(\rho D_z)}{\partial z} \right\} d\rho dz$$

$$= 2\pi \int_0 \rho \{D_\rho \cos(\rho, \nu) + D_z \cos(z, \nu)\} \, ds = 2\pi a \int_0 D_\nu ds$$

(3, 1)

$$\left\{ \begin{array}{l} i.e., \int_0 D_\nu ds = \frac{e}{2\pi a} = \eta \\ \text{Similarly,} \int_0 B_\nu ds = 0 \end{array} \right\}$$



Similarly

$$\int\int \left(\frac{\partial H_\rho}{\partial z} - \frac{\partial H_z}{\partial \rho} \right) 2\pi\rho d\rho dz = \int\int \eta v \delta \cdot 2\pi\rho d\rho dz = 2\pi a v \eta = ev$$

and the left-hand side

$$= 2\pi a \int_0 \{H_\rho \cos(z, \nu) - H_z \cos(\rho, \nu)\} \, ds$$

$$= -2\pi a \int_0 H_s \, ds$$

(3, 2)

$$\left\{ \begin{array}{l} i.e., \int_0 H_s ds = -\eta v \\ \text{Similarly,} \int_0 E_s ds = 0 \end{array} \right\}$$

4. Solution in the case of zero-approximation.

Take $\rho = a$.

In this case the equations

(4, 1) $$\frac{\partial B_\rho}{\partial \rho} + \frac{\partial B_z}{\partial z} = 0 \, ; \; \frac{\partial E_z}{\partial \rho} - \frac{\partial E_\rho}{\partial z} = 0$$

are satisfied by taking $B_\rho = \lambda E_z$ and $B_z = -\lambda E_\rho$, so that

$$B_\rho E_\rho + B_z E_z = 0$$

and the Lagrangian

$$L = b^2 \left\{ \sqrt{1 - \frac{1}{b^2}(1-\lambda^2)(E_\rho^2 + E_z^2)} - 1 \right\}$$

$$= b^2 \left\{ \sqrt{1 + \frac{1}{b^2}\left(1 - \frac{1}{\lambda^2}\right)(B_\rho^2 + B_z^2)} - 1 \right\}$$

or, without making these substitutions

$$L = b^2 \left\{ \sqrt{1 + \frac{1}{b^2}(B_\rho^2 + B_z^2 - E_\rho^2 - E_z^2)} - 1 \right\}$$

From this last form of L,

$$H_\rho = \frac{\partial L}{\partial B_\rho} = \frac{B_\rho}{\sqrt{1 + \frac{1}{b^2}(B_\rho^2 + B_z^2 - E_\rho^2 - E_z^2)}} = \frac{\lambda E_z}{\sqrt{\quad}}$$

$$= -\lambda \frac{\partial L}{\partial E_z} = \lambda D_z$$

Similarly $H_z = -\lambda D_\rho$.

These relations could also have been deduced from the relations

$$\frac{\partial H_z}{\partial \rho} - \frac{\partial H_\rho}{\partial z} = 0; \quad \frac{\partial D_\rho}{\partial \rho} + \frac{\partial D_z}{\partial z} = 0$$

and we would have obtained $H_\rho = \mu D_z$ and $H_z = -\mu D_\rho$; but, the above method however shows that $\mu = \lambda$.

We can determine λ from the boundary conditions

$$-\eta v = \int_0 H_s ds = \int_0 \{H_z \cos(\rho, \nu) - H_\rho \cos(z, \nu)\} ds$$

$$= -\lambda \int_0 \{D_\rho \cos(\rho, \nu) + D_z \cos(z, \nu)\} ds$$

$$= -\lambda \int D_\nu ds = -\lambda \eta$$

(4, 2) $\quad \therefore \quad \lambda = v.$ Let $1 - \lambda^2 = 1 - v^2 = \alpha^2$.

Rewriting the equations in the case of the zero-approximation

$$\frac{\partial D_\rho}{\partial \rho} + \frac{\partial D_z}{\partial z} = 0, \quad \frac{\partial E_z}{\partial \rho} - \frac{\partial E_\rho}{\partial z} = 0$$

with the boundary conditions

$$\int_0 D_\nu \, ds = \eta; \quad \int_0 E_s \, ds = 0$$

we find that a solution is given by

$$(4, 3) \qquad \left\{ \begin{array}{l} D_\rho = \dfrac{\eta}{2\pi r} \cdot \dfrac{\rho - a}{r} \\ \\ D_z = \dfrac{\eta}{2\pi r} \cdot \dfrac{z}{r} \end{array} \right\}$$

where $r^2 = (\rho - a)^2 + z^2$, *i.e.*, r is the distance from a point on the ring. We can easily express $\vec{E}$ in terms of $\vec{D}$ by considering the Hamiltonian H.

$$H = b^2 \left\{ \sqrt{1 + \frac{1}{b^2}(\vec{D}^2 - \vec{H}^2) - \frac{1}{b^4}(\vec{D}\,\vec{H})^2} - 1 \right\}$$

$$= b^2 \left\{ \sqrt{1 + \frac{1}{b^2}(\vec{D}^2 - \vec{H}^2)} - 1 \right\} \text{ since } (\vec{D}\,\vec{H}) = 0 \text{ in this case,}$$

as easily follows from the relation $H_\rho = \lambda D_z$ and $H_z = -\lambda D_\rho$.

$$\therefore E_\rho = \frac{\partial H}{\partial D_\rho} = \frac{D_\rho}{\sqrt{1 + \frac{1}{b^2}(\vec{D}^2 - \vec{H}^2)}} = \frac{D_\rho}{\sqrt{1 + \frac{a^2}{b^2}(D_\rho^2 + D_z^2)}}$$

and $$E_z = \frac{\partial H}{\partial D_z} = \frac{D_z}{\sqrt{1 + \frac{1}{b^2}(\vec{D}^2 - \vec{H}^2)}} = \frac{D_z}{\sqrt{1 + \frac{a^2}{b^2}(D_\rho^2 + D_z^2)}}$$

Putting in the values of D_ρ and D_z from (1)

$$(4, 4) \qquad \left\{ \begin{array}{l} E_\rho = \dfrac{\eta}{2\pi r} \cdot \dfrac{\rho - a}{\sqrt{r^2 + r_1^2}} \\ E_z = \dfrac{\eta}{2\pi r} \cdot \dfrac{z}{\sqrt{r^2 + r_1^2}} \end{array} \right\}$$

$$(4, 5) \qquad \text{where } r_1 = \frac{a\eta}{2\pi b}.$$

It is easy to verify that the E-equation, *viz.*, $\frac{\partial E_\rho}{\partial z} - \frac{\partial E_z}{\partial \rho} = 0$ is satisfied by the values (2). This needs only showing that

$$(\rho - a)\frac{\partial}{\partial z}\left\{\frac{1}{r\sqrt{r^2 + r_1^2}}\right\} = z\frac{\partial}{\partial \rho}\left\{\frac{1}{r\sqrt{r^2 + r_1^2}}\right\}$$

i.e., $$(\rho - a)\frac{\partial r}{\partial z} = z\frac{\partial r}{\partial \rho}$$

and this is true since $\frac{\partial r}{\partial z} = \frac{z}{r}$ and $\frac{\partial r}{\partial \rho} = \frac{\rho - a}{r}$.

From (2) $E = \frac{\eta}{2\pi} \cdot \frac{1}{\sqrt{r^2 + r_1^2}}$ and is finite for $r = 0$, having the value

$$(4, 6) \qquad \frac{\eta}{2\pi r_1} = \frac{b}{a} = b'.$$

We can now complete the solutions in the case of zero-approximation

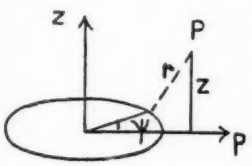
$$(4, 7) \qquad \left\{ \begin{array}{l} H_\rho = \dfrac{\eta v}{2\pi r} \cdot \dfrac{z}{r} \\ H_z = -\dfrac{\eta v}{2\pi r} \cdot \dfrac{\rho - a}{r} \end{array} \right\}$$

and

$$(4, 8) \qquad \left\{ \begin{array}{l} B_\rho = \dfrac{\eta v}{2\pi r} \cdot \dfrac{Z}{\sqrt{r^2 + r_1^2}} \\ B_z = -\dfrac{\eta v}{2\pi r} \cdot \dfrac{\rho - a}{\sqrt{r^2 + r_1^2}} \end{array} \right\}$$

5. Solutions in the classical case.

Treating the problem as the field due to a circular current, we have to determine the scalar and vector-potentials.



Referring to the adjoining figure the scalar potential ϕ is given by

$$\phi = \frac{1}{4\pi}\int_0^{2\pi} a d\psi \cdot \frac{\eta}{\sqrt{(\rho - a\cos\psi)^2 + a^2\sin^2\psi + z^2}}$$

$$i.e.,\ \phi = \frac{a}{4\pi}\int_0^{2\pi} \frac{\eta d\psi}{\sqrt{\rho^2 + z^2 - 2\rho a\cos\psi + a^2}}$$

$$= \frac{\eta a}{4\pi}\int_{\pi/2}^{-\pi/2} \frac{-2d\psi_0}{R\sqrt{1-k^2\sin^2\psi_0}}\ ;\ \text{where } R^2 = (\rho + a)^2 + z^2$$

$$k^2 = \frac{4\rho a}{R^2}\ ;\ \psi_0 = \frac{\pi - \psi}{2}$$

$$= \frac{\eta a}{\pi R}\int_0^{\pi/2} \frac{d\psi_0}{\sqrt{1 - k^2\sin^2\psi_0}}$$

$$(5,\ 1) \qquad \phi = a\eta\frac{K(k)}{\pi R} = \frac{e}{2\pi^2}\frac{K(k)}{R}$$

where $K(k)$ is the complete elliptic integral of the first kind.

Coming to a question of units, we observe that for $\rho, z \gg a$, (4) reduces to $\phi \to \frac{e}{4\pi R}$ since $K(0) = \pi/2$

i.e., the units we are using are the ordinary electrostatic units and *not* the Gaussian units. To transform to the latter we need only replace e by $4\pi e$. This fact shall be made use of later.

Coming to the vector-potential due to the circular current,[6] we have, denoting this by $\vec{A}$, $A_\rho = 0$, $A_z = 0$, and

$$(5,\ 2) \qquad A_\psi = \frac{\eta v}{\pi}\sqrt{\frac{a}{\rho}}\cdot\frac{1}{k}\left\{\left(1 - \frac{k^2}{2}\right)K(k) - E(k)\right\}$$

where $K(k)$ and $E(k)$ are the complete elliptic integrals of the 1st and 2nd kind.

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[6] See Debye, *Ency. Math. Wiss.*, V., **2**, § 17, p. 434.

From the potentials ϕ and $\vec{A}$, the field strengths are given by

$$\vec{E} = -\operatorname{grad}\phi; \quad \vec{H} = \operatorname{rot}\vec{A}$$

$$\left.\begin{aligned} i.e., \quad E_\rho &= -\frac{\partial\phi}{\partial\rho}; \; E_\psi = 0; \; E_z = -\frac{\partial\phi}{\partial z} \\ E_\rho &= -\frac{\partial A_\psi}{\partial z}; \; H_\psi = 0; \; H_z = \frac{1}{\rho}\frac{\partial}{\partial\rho}(\rho A_\psi) \end{aligned}\right\}$$

using (2, 5) and (2, 6)

From (4), we get

$$E_\rho = -\frac{\partial\phi}{\partial\rho} = \frac{a\eta}{\pi}\left[\frac{1}{R^2}\frac{\partial R}{\partial\rho}\cdot K(k) - \frac{1}{R}\cdot\frac{\partial K(k)}{\partial k}\cdot\frac{\partial k}{\partial\rho}\right]$$

$$R^2 = (\rho + a)^2 + Z^2; \; \frac{\partial R}{\partial\rho} = \frac{\rho + a}{R}; \; \frac{\partial R}{\partial z} = \frac{z}{R}$$

$$k^2 = \frac{4\rho a}{R^2}; \; \frac{1}{k}\frac{\partial R}{\partial\rho} = \frac{1}{2\rho} - \frac{\rho + a}{R^2}; \; \frac{1}{k}\frac{\partial k}{\partial z} = -\frac{z}{R^2}$$

From the theory of elliptic integrals,

$$\frac{\partial K(k)}{\partial k} = \frac{E(k)}{kk'^2} - \frac{K(k)}{k}$$

where k' is the modulus complementary to k, *i.e.*, $k'^2 = 1 - k^2$

$$i.e., \quad k'^2 = \frac{r^2}{R^2} \quad \text{or} \quad \underline{k' = \frac{r}{R}}$$

Hence,

$$E_\rho = \frac{a\eta}{\pi}\left[\frac{1}{R^2}\cdot\frac{\rho + a}{R}K(k) - \frac{1}{R}\left\{\left(\frac{E(k)R^2}{r^2} - K(k)\right)\left(\frac{1}{2\rho} - \frac{\rho + a}{R^2}\right)\right\}\right]$$

(5, 3)

$$i.e., \quad \left.\begin{aligned} E_\rho &= \frac{a\eta}{2\pi R\rho}\left\{K(k) - \frac{Z^2 + a^2 - \rho^2}{r^2}E(k)\right\} \\ E_z &= \frac{a\eta z}{\pi R r^2}E(k) \end{aligned}\right\}$$

Similarly

Coming now to the magnetic field strength, we get from (5, 2)

$$H_z = \frac{1}{\rho}\frac{\partial}{\partial\rho}(\rho A_\psi) = \frac{1}{\rho}\frac{\partial}{\partial\rho}\left[\frac{\eta v}{2\pi}\cdot R\left\{\left(1 - \frac{k^2}{2}\right)K(k) - E(k)\right\}\right]$$

$$H_z = \frac{\eta v}{2\pi\rho}\cdot\frac{\partial}{\partial\rho}\left[R\left\{\left(1 - \frac{k^2}{2}\right)K(k) - E(k)\right\}\right] \qquad \left[\frac{\partial E(k)}{\partial k} = \frac{E(k) - K(k)}{k}\right.$$

$$= \frac{\eta v}{2\pi\rho}\left[\frac{\partial R}{\partial\rho}\left\{\left(1 - \frac{k^2}{2}\right)K(k) - E(k)\right\} + R\left\{\left(1 - \frac{k^2}{2}\right)\frac{\partial K(k)}{\partial k}\cdot\frac{\partial k}{\partial\rho}\right.\right.$$

$$\left.\left. - K(k)\cdot k\frac{\partial k}{\partial\rho} - \frac{\partial E(k)}{\partial k}\cdot\frac{\partial k}{\partial\rho}\right\}\right]$$

$$= \frac{\eta v}{2\pi\rho}\left[\frac{\rho+a}{R}\left\{K(k) - \frac{E(k)}{k'^2}\left(1-\frac{k^2}{2}\right)\right\} + \frac{R}{2\rho}\left\{\frac{E(k)}{k'^2}\left(1-\frac{k^2}{2}-k'^2\right) - K(k)\frac{k^2}{2}\right\}\right]$$

Putting $k^2 = 4a\rho/R^2$, $k'^2 = r^2/R^2$, this reduces to

$$H_z = \frac{\eta v}{2\pi\rho}\left[\frac{\rho}{R}K(k) + E(k)\left\{\frac{aR}{r^2} - \frac{(\rho+a)(\rho^2+a^2+z^2)}{Rr^2}\right\}\right]$$

$$= \frac{\eta v}{2\pi\rho}\left[\frac{\rho}{R}K(k) - \frac{E(k)\rho}{Rr^2}(\rho^2 - a^2 + z^2)\right]$$

$$= \frac{\eta v\rho}{2\pi\rho R}\left\{K(k) - \frac{\rho^2 - a^2 + z^2}{r^2}E(k)\right\}$$

Similarly,

$$H_\rho = -\frac{\partial A_\psi}{\partial z} = -\frac{\partial}{\partial z}\left[\frac{\eta v}{2\pi}\cdot\frac{R}{\rho}\left\{\left(1-\frac{k^2}{2}\right)K(k) - E(k)\right\}\right]$$

$$= -\frac{\eta v}{2\pi\rho}\frac{\partial}{\partial z}\left[R\left\{\left(1-\frac{k^2}{2}\right)K(k) - E(k)\right\}\right]$$

$$= -\frac{\eta v}{2\pi\rho}\left[\frac{\partial R}{\partial z}\left\{\left(1-\frac{k^2}{2}\right)K(k) - E(k)\right\} + R\left\{\left(1-\frac{k^2}{2}\right)\frac{\partial K(k)}{\partial k}\cdot\frac{\partial k}{\partial z} - kK(k)\frac{\partial k}{\partial z} - \frac{\partial E(k)}{\partial k}\cdot\frac{\partial k}{\partial z}\right\}\right]$$

$$= -\frac{\eta v}{2\pi\rho}\left[\frac{Z}{R}\left\{K(k) - \frac{E(k)}{k'^2}\left(1-\frac{k^2}{2}\right)\right\}\right]$$

simplifying by substituting the expressions for $\frac{\partial K(k)}{\partial k}$ and $\frac{\partial E(k)}{\partial k}$.

$$= -\frac{\eta v z}{2\pi R\rho}\left\{K(k) - \frac{\rho^2 + a^2 + Z^2}{r^2}E(k)\right\};$$

thus,

$$(5,4)\qquad \left\{\begin{aligned} H_\rho &= -\frac{\eta v z}{2\pi R\rho}\left\{K(k) - \frac{\rho^2+a^2+z^2}{r^2}E(k)\right\} \\ H_z &= \frac{\eta v}{2\pi R}\left\{K(k) - \frac{\rho^2+a^2+z^2}{r^2}\right\}E(k) \end{aligned}\right\}$$

In (5, 3) and (5, 4) we can transform the expressions

$$\frac{z^2+a^2-\rho^2}{r^2},\quad \frac{\rho^2+a^2+z^2}{r^2},\quad \frac{\rho^2-a^2+z^2}{r^2}$$

by writing $z^2 = r^2 - (\rho - a)^2$ and obtain

$$(5,5)\qquad \left\{\begin{aligned} E_\rho &= \frac{a\eta}{\pi R}\cdot\frac{\rho-a}{r^2}E(k) + \frac{a\eta}{2\pi R\rho}[K(k) - E(k)] \\ E_z &= \frac{a\eta}{\pi R}\cdot\frac{z}{r^2}E(k) \end{aligned}\right\}$$

$$(5,\ 6)\qquad \left\{\begin{array}{l} H_\rho = \dfrac{a\eta v}{\pi R}\cdot\dfrac{z}{r^2}\,E(k) - \dfrac{\eta v z}{2\pi R\rho}\,[K(k) - E(k)] \\ \\ H_z = -\dfrac{a\eta v}{\pi R}\cdot\dfrac{\rho - a}{r^2}\,E(k) + \dfrac{\eta v}{2\pi R}\,[K(k) - E(k)] \end{array}\right\}$$

(5, 5) and (5, 6) are the exact classical solutions (where $\vec{B} = \vec{H}$ and $\vec{D} = \vec{E}$). Going to the limit $r \to 0$ which corresponds to the case $\rho = a$, $z = 0$, *i.e.*, on the ring, we have

$$R \to 2a,\ k' \to 0, \text{ and}$$

$$E(k) \to 1 \text{ and } K(k) \to \log((4/k').$$

Hence the classical solutions valid in the neighbourhood of the ring are

$$(5,\ 7)\qquad \left\{\begin{array}{l} E_\rho = \dfrac{\eta}{2\pi}\cdot\dfrac{\rho - a}{r^2} + \dfrac{\eta}{4\pi a}\left(\log\dfrac{8a}{r} - 1\right) \\ \\ E_z = \dfrac{\eta}{2\pi}\cdot\dfrac{Z}{r^2} \end{array}\right\}$$

and,

$$(5,\ 8)\qquad \left\{\begin{array}{l} H_\rho = \dfrac{\eta v}{2\pi}\cdot\dfrac{z}{r^2} \\ \\ H_z = -\dfrac{\eta v}{2\pi}\cdot\dfrac{\rho - a}{r^2} + \dfrac{\eta v}{4\pi a}\left(\log\dfrac{8a}{r} - 1\right) \end{array}\right\}$$

It is interesting to observe that the first terms in the right-hand members of (5, 7) and (5, 8) agree with the unitary field theory expression for the zero approximation case (4, 3), (4, 4), (4, 7), (4, 8) when, in the latter, we consider (r_1/r) small and neglect second and higher powers.

6. *Method of procedure for calculating integrals of energy and angular momentum.*

The remarks made above suggest the method of procedure to be adopted for the calculation of these integrals. We assume that the classical solutions hold good except in the immediate neighbourhood of the ring where we assume the field theory solutions (in §4) to be valid for values of r large compared with r_1. Thus, in the case of the total energy E, for example, we form the classical and field theory expressions U_{cl} and U_f and write

$$(6,\ 1)\qquad E = \int U_{cl}\,dV + U_f\,dV$$

Since we can certainly assume that most of the energy is concentrated in the neighbourhood of the ring we take the limits for r in the first integral $r =$ a finite number $= f$ (say) for the upper limit and r for the lower limit such that *r is small compared with a*. The limit f is further so chosen that no terms appear after integration which $\to \infty$ as $r \to \infty$. For the second

integral the lower limit is taken 0 while the upper limit r is assumed *large compared with* r_1 but small compared with a. The angular momentum is similarly treated. Further in calculating U_f we use the expressions in §4 and for U_{cl} the expressions (5, 7) – (5, 8), or, in case a higher approximation is needed, the expressions (5, 5) and (5, 6) with the substitution therein, up to the desired degree of accuracy, from the series—expansions for K (k) and E (k)[7] valid in the neighbourhood of $k = 1$, or $k' = 0$, *viz.*,

$$(6, 2) \qquad \begin{cases} \mathrm{E}(k) = 1 + \dfrac{k'^2}{2}\left(\log \dfrac{4}{k'} - \dfrac{1}{2}\right) + \dfrac{3}{16}\,k'^4\left(\log \dfrac{4}{k'} - 1 - \dfrac{1}{12}\right) + \cdots \\ \mathrm{K}(k) = \log \dfrac{4}{k'} + \dfrac{k'^2}{2}\left(\log \dfrac{4}{k'} - 1\right) + \cdots \end{cases}$$

7. *Calculation of the energy.*

$$\mathrm{U}_f = \mathrm{I}_4 + (\vec{\mathrm{D}}\cdot\vec{\mathrm{E}})$$

$$= b^2\left\{\sqrt{1 + \frac{1}{b^2}\,(\vec{\mathrm{B}}^2 - \vec{\mathrm{E}}^2)} - 1\right\} + \vec{\mathrm{D}}\,\vec{\mathrm{E}}, \text{ since } (\vec{\mathrm{B}}\cdot\vec{\mathrm{E}}) = 0 \text{ from §(4).}$$

$$= b^2\left\{\sqrt{1 + \frac{1}{b^2}\left(\frac{\eta^2 v^2}{4\pi^2 r^2}\cdot\frac{r^2}{r^2 + r_1^2} - \frac{\eta^2}{4\pi^2 r^2}\cdot\frac{r^2}{r^2 + r_1^2}\right)} - 1\right\} + \frac{\eta^2}{4\pi^2 r^2}\cdot\frac{1}{\sqrt{r^2 + r_1^2}}$$

$$= b^2\left\{\sqrt{1 - \frac{r_1^2}{r^2 + r_1^2}} - 1\right\} + \frac{b^2 r_1^2}{a^2 r\,\sqrt{r^2 + r_1^2}}, \text{ using (4, 5)}$$

$$\therefore \int \mathrm{U}_f\, dV = 2\pi \iint \mathrm{U}_f \rho d\rho dz$$

$$= 2\pi \int_0^r \int_0^{2\pi} \mathrm{U}_f\,(a + r\cos\phi)\, r dr d\phi$$

$$= 2\pi a \int_0^r \int_0^{2\pi} \mathrm{U}_f\, r dr d\phi$$

since $\int_0^{2\pi} \cos\phi \cdot d\phi = 0$, and U_f is a function of r only.

We have here taken r and ϕ to be polar co-ordinates in the meridian plane, such that,

$$(7, 1) \qquad \begin{cases} \rho - a = r\cos\phi \\ z = r\sin\phi \\ d\rho dz = r dr d\phi \end{cases}$$

[7] See, for example, Schlomilch, *Komp. d. Hoh. Anal.*, Bd. 2, pp. 322–323.

$$i.e., \quad \int U_f \, dV = 4\pi^2 a \int_0^r U_f \, r dr$$

$$= 4\pi^2 \, ab^2 \int_0^r \left[\left\{ \sqrt{1 - \frac{r_1^2}{r^2 + r_1^2}} - 1 \right\} + \frac{r_1^2}{a^2 r \sqrt{r^2 + r_1^2}} \right] r dr$$

$$= 4\pi^2 \, ab^2 \int_0^r \left\{ \frac{r^2}{\sqrt{r^2 + r_1^2}} - r + \frac{r_1^2}{a^2 \sqrt{r^2 + r_1^2}} \right\} dr$$

$$= 4\pi^2 \, ab^2 \int_0^r \left(\sqrt{r^2 + r_1^2} - \frac{r_1^2}{\sqrt{r^2 + r_1^2}} - r \right) dr + 4\pi^2 \, ab'^2 \int_0^r \frac{r_1^2 \, dr}{\sqrt{r^2 + r_1^2}}$$

$$= 4\pi^2 \, ab^2 \int_0^r (\sqrt{r^2 + r_1^2} - r) \, dr + 4\pi^2 a \, (b'^2 - b^2) \int_0^r \frac{r_1^2 \, dr}{\sqrt{r^2 + r_1^2}}$$

$$= a\eta^2 \, a^2 \int_0^x (\sqrt{1 + x^2} - x) \, dx + a\eta^2 v^2 \int_0^x \frac{dx}{\sqrt{1 + x^2}}$$

putting $r = r_1 x$ and using $r_1 = \frac{a\eta}{2\pi b}$; $b' = \frac{b}{a}$.

$$= \tfrac{1}{2} \, a\eta^2 \alpha^2 \left\{ \frac{r}{r_1} \sqrt{1 + \frac{r^2}{r_1^2}} - \frac{r^2}{r_1^2} \right\} + \tfrac{1}{2} \, a\eta^2 \beta^2 \log \left\{ \frac{r}{r_1} + \sqrt{1 + \frac{r^2}{r_1^2}} \right\}$$

(7. 2) where $\beta^2 = 1 + v^2$

$$(7, 3) \qquad \int U_f \, dV = a\eta^2 \log \left(\frac{2r}{r_1} \right)$$

where we have made use of the fact that r is large compared with r_1 and that *v is very nearly equal to the velocity of light, i.e., unity.*

We now proceed to calculate the classical part of the energy and write, making use of (5, 7)-(5, 8),

$$U_{cl} = \tfrac{1}{2} (\vec{E}^2 + \vec{H}^2) = \tfrac{1}{2} (\vec{E}_\rho^2 + E_z^2 + H_\rho^2 + H_z^2)$$

$$= \frac{\eta^2 \beta^2}{8\pi^2 r^2} + \frac{\eta^2 \beta^2}{32\pi^2 a^2} \left(\log \frac{8a}{r} - 1 \right)^2 + \frac{\eta^2 \alpha^2}{8\pi^2 a} \cdot \frac{\rho - a}{r^2} \left(\log \frac{8a}{r} - 1 \right)$$

$$\therefore \quad \int U_{cl} \, dV = \tfrac{1}{2} \, a\eta^2 \beta^2 \int_r^f \frac{dr}{r} + \frac{\eta^2 \beta^8}{8a} \int r \left(\log \frac{8a}{r} - 1 \right)^2 dr + \frac{\eta^2 \alpha^2}{8\pi^2 a}$$

$$\int \int \frac{\rho - a}{r^2} \left(\log \frac{8a}{r} - 1 \right) 2\pi \rho d\rho dz$$

$$\int\int \frac{\rho - a}{r^2}\left(\log\frac{8a}{r} - 1\right) 2\pi\rho d\rho dz = \int_r^f \int_0^{2\pi} \frac{r\cos\phi}{r^2}\left(\log\frac{8a}{r} - 1\right) 2\pi\,(a + r\cos\phi)\, r dr d\phi$$

$$= \int_r^f \int_0^{2\pi} 2\pi r\left(\log\frac{8a}{r} - 1\right)\cos^2\phi dr d\phi$$

$$= \int_r^f 2\pi^2 r\left(\log\frac{8a}{r} - 1\right) dr$$

Now,

$$\int r\left(\log\frac{8a}{r} - 1\right)^2 dr = \frac{r^2}{2}\left(\log\frac{8a}{r} - 1\right)^2 + \frac{r^2}{2}\left(\log\frac{8a}{r} - 1\right) + \frac{r^2}{4} = \frac{r^2}{2}\left(\log\frac{8a}{r}\right)^2 - \frac{r^2}{2}\log\frac{8a}{r} + \frac{r^2}{4}$$

and $\int r\left(\log\frac{8a}{r} - 1\right)dr = \frac{r^2}{2}\left(\log\frac{8a}{r} - 1\right) + \frac{r^2}{4} = \frac{r^2}{2}\left(\log\frac{8a}{r}\right) - \frac{r^2}{4}$

To avoid infinites at the upper limit we put $f = 8a$ and get

$$\int U_{el}\, dV = \tfrac{1}{2}\, a\eta^2\beta^2 \log\frac{8a}{r} + 0\,(r\log r) + 0\,(r^2\log r) + 0\,(r^2).$$

Since $\underset{r\to 0}{\text{Lt}}\,(r\log r) = \underset{r\to 0}{\text{Lt}}\,(r^2\log r) = \underset{r\to 0}{\text{Lt}}\,(r^2) = 0$ and r is small compared with a, we can neglect the last three terms and write

$$(7,\,4)\qquad \int U_{el}\, dV = \tfrac{1}{2}\, a\eta^2\beta^2 \log\frac{8a}{r} = a\eta^2 \log\frac{8a}{r}$$

From (7, 3) and (7, 4), we get

$$E = a\eta^2 \log\left(\frac{2r}{r_1}\right) + a\eta^2 \log\left(\frac{8a}{r}\right)$$

$$(7,\,5)\quad \textit{i.e.,}\ E = a\eta^2 \log\left(\frac{16a}{r_1}\right)$$

giving a finite value for the energy.

8. Calculation of the angular momentum.

Corresponding to (6, 1) we write

$$(8,\,1)\qquad \vec{M} = \int \vec{M}_{el} dV + \int \vec{M}_f\, dV.$$

$$\vec{M} = \int \{\vec{r} \times (\vec{D} \times \vec{B})\}\, dV$$

$$= \int \{\vec{D}\,(\vec{r}\,\vec{B}) - \vec{B}\,(\vec{r}\,\vec{D})\}\, dV$$

$$\left.\begin{aligned} \therefore\quad \mathrm{M}_\rho &= \int \{\mathrm{Z}\,(\mathrm{D}_\rho \mathrm{B}_z - \mathrm{B}_\rho \mathrm{D}_z)\}\, d\mathrm{V} \\ \mathrm{M}_z &= \int \{\rho\,(\mathrm{D}_z \mathrm{B}_\rho - \mathrm{B}_z \mathrm{D}_\rho)\}\, d\mathrm{V} \\ \mathrm{M}_\phi &= 0 \end{aligned}\right\}$$

From the fact of axial symmetry, or observing that the integrand in M_ρ changes sign when z is replaced by $-z$, we have $\mathrm{M}_\rho = 0$ and $\mathrm{M} = \mathrm{M}_z$. Hence

$$\int \mathrm{M}_f\, d\mathrm{V} = \int \rho\,(\mathrm{D}_z \mathrm{B}_\rho - \mathrm{B}_z \mathrm{D}_\rho)\, d\mathrm{V}$$

$$= \frac{\eta^2 v}{4\pi^2} \int \frac{\rho}{r\sqrt{r^2 + r_1^2}}\, d\mathrm{V}$$

using (4, 3) and (4, 8)

$$i.e.,\quad \int \mathrm{M}_f\, d\mathrm{V} = \frac{\eta^2 v}{4\pi^2} \int\int \frac{\rho \cdot 2\pi\rho d\rho dz}{r\sqrt{r^2 + r_1^2}}$$

$$= \frac{\eta^2 v}{2\pi} \int_0^r \int_0^{2\pi} \frac{(a + r\cos\phi)^2\, r dr d\phi}{r\sqrt{r^2 + r_1^2}}$$

$$= \frac{\eta^2 v}{2\pi} \int_0^r \frac{dr}{\sqrt{r^2 + r_1^2}}\,(2\pi a^2 + \pi r^2)$$

$$= \eta^2 v \int_0^r \frac{a^2 dr}{\sqrt{r^2 + r_1^2}} + \frac{\eta^2 v}{2} \int_0^r \frac{r^2 dr}{\sqrt{r^2 + r_1^2}}$$

$$= \eta^2 v a^2 \int_0^r \frac{dr}{\sqrt{r^2 + r_1^2}} + \frac{\eta^2 v}{2} \int_0^r \sqrt{r^2 + r_1^2}\, dr - \frac{\eta^2 v r_1^2}{2} \int_0^r \frac{dr}{\sqrt{r^2 + r_1^2}}$$

$$= \frac{\eta^2 v}{2} \int_0^r \sqrt{r^2 + r_1^2}\, dr + \frac{\eta^2 v}{2}\,(2a^2 - r_1^2) \int_0^r \frac{dr}{\sqrt{r^2 + r_1^2}}$$

$$= \frac{\eta^2 v r_1^2}{2} \int_0^x \sqrt{1 + x^2}\, dx + \frac{\eta^2 v}{2}\,(2a^2 - r_1^2) \int_0^x \frac{dx}{\sqrt{1 + x^2}}$$

$$= \frac{\eta^2 v r_1^2}{2}\,[\tfrac{1}{2} x\sqrt{1 + x^2} + \tfrac{1}{2} \log\,(x + \sqrt{1 + x^2})]$$

$$+ \frac{\eta^2 v}{2}\,(2a^2 - r_1^2) \log\,(x + \sqrt{1 + x^2})$$

$$= \frac{\eta^2 v}{2}\left(2a^2 - \frac{r_1^2}{2}\right) \log\left(\frac{r}{r_1} + \sqrt{1 + \frac{r^2}{r_1^2}}\right) + \frac{\eta^2 v r\,\sqrt{r^2 + r_1^2}}{4}$$

$$= \eta^2 v a^2 \log\left(\frac{r}{r_1} + \sqrt{1 + \frac{r^2}{r_1^2}}\right) + \frac{\eta^2 v}{4}\, r\,\sqrt{r^2 + r_1^2}$$

neglecting the term in r_1^2

$$(8,\ 2) \qquad \int \mathrm{M}_f\, d\mathrm{V} = \eta^2 v a^2 \log\left(\frac{2r}{r_1}\right) + \frac{\eta^2 v}{4}\, r^2$$

since r is assumed large compared with r_1.

On the classical theory.

$$\mathrm{M}_z = \int \rho\, (\mathrm{E}_z\, \mathrm{H}_\rho - \mathrm{H}_z\, \mathrm{E}_\rho)\, d\mathrm{V}$$

Using the exact expressions (5, 5)-(5, 6) we have

$$\mathrm{E}_z\mathrm{H}_\rho - \mathrm{H}_z\mathrm{E}_\rho = \frac{a\eta}{\pi \mathrm{R}} \cdot \frac{z}{r^2}\, \mathrm{E}(k) \left\{\frac{a\eta v}{\pi \mathrm{R}} \cdot \frac{z}{r^2}\, \mathrm{E}(k) - \frac{\eta v z}{2\pi \mathrm{R}\rho}\, [\mathrm{K}(k) - \mathrm{E}(k)]\right\}$$
$$- \left\{\frac{a\eta}{\pi \mathrm{R}} \cdot \frac{\rho - a}{r^2}\, \mathrm{E}(k) + \frac{a\eta}{2\pi \mathrm{R}\rho}\Big(\mathrm{K}(k) - \mathrm{E}(k)\Big)\right\} \left\{-\frac{a\eta v}{\pi \mathrm{R}} \cdot \frac{\rho - a}{r^2}\, \mathrm{E}(k) + \frac{\eta v}{2\pi \mathrm{R}}\, \mathrm{K}(k) - \mathrm{E}(k)\right\}$$

$$= \frac{a\eta^2 v}{\pi^2 \mathrm{R}^2}\left[\left\{a\mathrm{E}^2 \frac{z^2}{r^4} - \frac{1}{2\rho} \cdot \frac{z^2}{r^2}\, \mathrm{E}(\mathrm{K} - \mathrm{E})\right\} + \left\{\left(\frac{\rho - a}{r^2}\, \mathrm{E} + \frac{1}{2\rho}\, \overline{\mathrm{K} - \mathrm{E}}\right)\left(\overline{\frac{a\ \rho - a}{r^2}}\, \mathrm{E} - \tfrac{1}{2}\, \overline{\mathrm{K} - \mathrm{E}}\right)\right\}\right]$$

$$= \frac{a\eta^2 v}{\pi^2 \mathrm{R}^2}\left[\left\{a\mathrm{E}^2 \frac{z^2}{r^4} - \frac{1}{2\rho} \frac{z^2}{r^2}\, \mathrm{E}\,(\mathrm{K} - \mathrm{E})\right\} + \left\{a\mathrm{E}^2 \frac{(\rho - a)^2}{r^4} + \mathrm{E}\,(\mathrm{K} - \mathrm{E})\left(\frac{a}{2\rho} \cdot \frac{\rho - a}{r^2} - \frac{\rho - a}{2r^2}\right) - \frac{1}{4\rho}\,(\mathrm{K} - \mathrm{E})^2\right\}\right]$$

$$= \frac{a\eta^2 v}{\pi^2 \mathrm{R}^2}\left\{\frac{a\mathrm{E}^2}{r^2} - \frac{\mathrm{E}(\mathrm{K} - \mathrm{E})}{2\rho} - \frac{1}{4\rho}\,(\mathrm{K} - \mathrm{E})^2\right\}$$

$$= \frac{a\eta^2 v}{\pi^2 \mathrm{R}^2}\left\{\frac{a\mathrm{E}^2}{r^2} + \frac{\mathrm{E}^2}{2\rho} - \frac{\mathrm{EK}}{2\rho} + \frac{\mathrm{EK}}{2\rho} - \frac{\mathrm{K}^2}{4\rho} - \frac{\mathrm{E}^2}{4\rho}\right\}$$

$$= \frac{a\eta^2 v}{\pi^2 \mathrm{R}^2}\left\{\left(\frac{a}{r^2} + \frac{1}{4\rho}\right)\mathrm{E}^2 - \frac{1}{4\rho}\,\mathrm{K}^2\right\}$$

$$= \frac{a\eta^2 v}{4\pi^2 \rho \mathrm{R}^2}\left\{\frac{\mathrm{R}^2}{r^2}\,\mathrm{E}^2 - \mathrm{K}^2\right\}$$

$$(8,\ 3) \quad \therefore \quad \rho\,(\mathrm{E}_z\mathrm{H}_\rho - \mathrm{H}_z\,\mathrm{E}_\rho) = \frac{a\eta^2 v}{4\pi^2 \mathrm{R}^2}\left\{\frac{[\mathrm{E}(k)]^2}{k'^2} - [\mathrm{K}(k)]^2\right\}$$

Before proceeding further with the approximations for E (k) and K (k) valid in the neighbourhood of the ring, we might notice the very elegant form (8, 3) for the angular-momentum, this being the exact expression. It might also be observed that (8, 3) shows directly that Mρ is an odd function of z, for, the expression

$$\mathrm{E}_\rho\mathrm{H}_z - \mathrm{H}_\rho\mathrm{E}_z = \frac{a\eta^2 v}{4\pi^2 \mathrm{R}^2}\left\{[\mathrm{K}(k)]^2 - \frac{[\mathrm{E}(k)]^2}{k'^2}\right\}$$

is an even function of z, since only squares of E (k), K (k), k' and R appear in it and further k, k', r and R are all even functions of Z. Hence the expression

$$Z\,(E_\rho H_z - H_\rho E_z) \text{ is an odd function of Z.}$$

We now proceed with the approximation of (8, 3) by writing

$$E\,(k) = 1 + \frac{k'^2}{2}\left(\log\frac{4}{k'} - \tfrac{1}{2}\right) + \frac{3}{16}\,k'^4\left(\log\frac{4}{k'} - 1 - \frac{1}{12}\right)$$

and $\quad K\,(k) = \log\frac{4}{k'} + \frac{k'^2}{4}\left(\log\frac{4}{k'} - 1\right)$, and get

$$\frac{E^2}{k'^2} - K^2 = \frac{1}{k'^2} + \left\{\log\frac{4}{k'} - \tfrac{1}{2} - \left(\log\frac{4}{k'}\right)^2\right\} + k'^2\left\{-\tfrac{1}{4}\left(\log\frac{4}{k'}\right)^2 + \frac{5}{8}\log\frac{4}{k'} - \frac{11}{32}\right\}$$

and this does not depend on ϕ; hence

$$\int M_{cl}\,dV = \int \rho\,(E_z H_\rho - H_z E_\rho)\,dV$$

$$= a^2\eta^2 v \int_r^f \frac{1}{R^2}\left(\frac{R^2}{r^2}\,[E(k)]^2 - [K(k)]^2\right) r\,dr$$

$$= a^2\eta^2 v \int \left\{\frac{[E(k)]^2}{r^2} - \frac{[K(k)]^2}{R^2}\right\} r\,dr$$

Substituting the series-expansions for E (k), K (k) and $R = 2a$ and proceeding with the integration as in the case of the energy we take $f = 8a$. We neglect as before, the terms $(r \log r)$ and $(r^2 \log r)$ at the lower limit but retain the term in r^2, in view of the form of expression (8, 2). This gives

$$(8, 4) \qquad \int M_{cl}\,dV = a^2\eta^2 v \log\left(\frac{8a}{r}\right) - \frac{\eta^2 v}{4}\,r^2$$

From (8, 2) and (8, 4) we get easily

$$(8, 5) \qquad M = a^2\eta^2 v \log\,(16a/r_1)$$

giving *a finite value for the angular-momentum as well.*

[A simpler way of deducing (8, 5) would have been to neglect the terms in r^2 both in (8, 2) and (8, 4) since in both cases r^2 appears as an absolute term.]

9. *Magnetic moment.*

The magnetic moment can be calculated from the expression (5, 2) for the classical vector-potential, *viz.*,

$$A_\phi = \frac{\eta v}{\pi}\sqrt{\frac{a}{\rho}}\cdot\frac{1}{k}\left\{\left(1 - \frac{k^2}{2}\right)K(k) - E(k)\right\}$$

For values of $k \ll 1$, *i.e.*, at great distance from the ring,[8]

$$\begin{aligned} A_\psi &= \frac{\eta v}{32}\sqrt{\frac{a}{\rho}} \cdot R^3 \left\{1 + \frac{3}{4}k^2 + - -\right\} \\ &= \frac{\eta v}{32}\sqrt{\frac{a}{\rho}} \cdot \frac{8\sqrt{a\rho}\cdot a\rho}{R^3}\left\{1 + \frac{3}{4}\cdot\frac{4\rho a}{R^2} + - -\right\} \\ &= \frac{a^2\eta v}{4}\cdot\frac{\rho}{R^3}\left\{1 + \frac{3\rho a}{R^2} + - -\right\} \end{aligned}$$

Hence the magnetic moment

$$(9,1)\quad m = \frac{a^2\eta v}{4} = \frac{a^2 e v}{8\pi a} = \frac{aev}{8\pi}$$

10. Spin.

We shall write the expressions for the energy, angular momentum and magnetic moment in Gaussian units since we have so far used only electrostatic units (also $c = 1$). This requires as remarked on p. 363, the replacing of e by $4\pi e$ *i.e.*, η by $4\pi\eta$.

$$(10,1)\quad E = a\eta^2 \log\left(\frac{16a}{r_1}\right) = \frac{ae^2}{4\pi^2 a^2}\log\left(\frac{16a}{r_1}\right) \longrightarrow \frac{4e^2}{a}\log\left(\frac{16a}{r_1}\right)$$

$$(10,2)\quad M = a^2\eta^2 v \log\left(\frac{16a}{r_1}\right) = \frac{e^2 v}{4\pi^2}\log\left(\frac{16a}{r_1}\right) \longrightarrow 4e^2 v \log\left(\frac{16a}{r_1}\right)$$

$$(10,3)\quad m = \frac{a^2\eta v}{4} = \frac{a^2 e v}{8\pi a} = \frac{aev}{8\pi} \longrightarrow \frac{aev}{2}$$

Hence $$\frac{E}{M} = \frac{1}{av} = \frac{e}{2m}$$ and,

putting $E = \mu c^2$ we have $E = \mu$ since $c = 1$, which gives

$$(10,4)\qquad \frac{m}{M} = \frac{e}{2\mu}$$

showing that if the particle represented by the ring-singularity be an electron, *the spin of the electron is not explained* by our classical method of investigation.

11. The mass of the proton.

If we consider the ring-singularity to represent the proton it can be shown that we can derive an estimate of the ring-radius which would give the right proton mass.

Equating (10, 2) to $\hbar = h/2\pi$, we get

$$\frac{h}{2\pi} = 4e^2 v \log\left(\frac{16a}{r_1}\right)$$

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[8] *Cf.* Debye, *ibid.*, p. 435.

where r_1 is given from (4, 5), using Gaussian-units, as

$$r_1 = \frac{ae}{\pi ab} = \sqrt{1-v^2} \cdot \frac{e}{\pi ba}$$

Introducing now the radius r_0 of the point charge of the field theory,[9] which is given by $e = br_0^2$, we have

$$r_1 = \sqrt{1-v^2}\,\frac{r_0^2}{\pi a}$$

and

$$\frac{16a}{r_1} = \frac{16\pi a^2}{r_0^2} \cdot \frac{1}{\sqrt{1-v^2}} = 16\pi \left(\frac{a}{r_0}\right)^2 \frac{1}{\sqrt{1-v^2}}$$

and (10, 2) gives

$$\frac{h}{2\pi} = 4e^2 v \log \left\{ 16\pi \left(\frac{a}{r_0}\right)^2 \cdot \frac{1}{\sqrt{1-v^2}} \right\}$$

Introducing c, instead of taking $c = 1$, this can be written in the form

$$(11, 1) \quad \frac{\hbar c}{e^2} = \frac{4v}{c} \log \left\{ 16\pi \left(\frac{a}{r_0}\right)^2 \frac{1}{\sqrt{1-v^2/c^2}} \right\}$$

We can similarly write the expression for the energy (10, 1) in the form

$$(11, 2) \quad \mathrm{E} = \frac{4e^2}{a} \log \left\{ 16\pi \left(\frac{a}{r_0}\right)^2 \frac{1}{\sqrt{1-v^2/c^2}} \right\}$$

Let m_0 = mass of a point charge and M_0 = mass of the ring, which we now assume to represent the mass of the proton. We have[10]

$$(11, 3) \quad 1{\cdot}236\,\frac{e^2}{r_0} = m_0 c^2$$

Putting $\mathrm{E} = \mathrm{M}_0 c^2$ in (11, 2) and making use of (11, 3) we get

$$(11, 4) \quad \frac{\mathrm{M}_0}{m_0} = \frac{\mathrm{E}}{1{\cdot}236e^2/r_0} = \frac{4r_0}{1{\cdot}236a} \log \left[\frac{16\pi}{a} \left(\frac{a}{r_0}\right)^2 \right]$$

From the equations (11, 1) and (11, 4) we can determine v/c and r_0/a if we observe that the left-hand side of (11, 1) is the fine structure constant whose value we shall take as 137 and that the left-hand side of (11, 4) is the ratio of the masses of proton and electron which we shall take as 1840. Thus

$$\frac{4r_0}{1{\cdot}236a} \log \left[\frac{16\pi}{a} \left(\frac{a}{r_0}\right)^2 \right] = 1840 \text{ from (11, 4), or}$$

$$(11, 5) \quad \frac{4r_0}{a} \log \left[\frac{16\pi}{a} \left(\frac{a}{r_0}\right)^2 \right] = 2274, \text{ and}$$

$$(11, 6) \quad \frac{4v}{c} \log \left[\frac{16\pi}{a} \left(\frac{a}{r_0}\right)^2 \right] = 137$$

---

[9] Born and Infeld, *Proc. Roy. Soc.*, A, 1934, **144**, p. 439.

[10] *Ibid.*, p. 446, equation (8, 7).

We can solve the equations (11, 5) and (11, 6) for v/c and r_0/a. Denoting these by x and y, the above equations can be written in the form

$$\left.\begin{aligned} &(11, 7) \quad 4x \log\left(\frac{16\pi}{x^2\sqrt{1-y^2}}\right) = 2274 \\ &(11, 8) \quad 4y \log\left(\frac{16\pi}{x^2\sqrt{1-y^2}}\right) = 137 \end{aligned}\right\}$$

The second equation can be written in the form (using only the nearest integers)

$$\frac{16\pi}{x^2\sqrt{1-y^2}} = \epsilon^{34/y} \quad (\epsilon \text{ is the exponential})$$

$$(11, 9) \quad x^2 = \frac{16\pi}{\sqrt{1-y^2}}\,\epsilon^{-34/y}$$

Dividing (11, 8) by (11, 7), we have

$$(11, 10) \quad \frac{y}{x} = \frac{137}{2274} \text{ or } y = \frac{x}{17}$$

Hence eliminating x between (11, 9) and (11, 10)

$$y = \frac{4\sqrt{\pi}}{17} \cdot \frac{1}{(1-y^2)}\,\tfrac{1}{4}\,\epsilon^{-17/y}$$

$$(11, 11) \quad i.e., \; y\,(1-y^2)^{\frac{1}{4}} = \frac{8}{11}\,\epsilon^{-17/y}$$

From this equation we can estimate how near the value of y is to unity. Putting $1 - y^2 = \epsilon_0^4$ (ϵ_0 an infinitesimal) the order of magnitude of ϵ_0 is determined by

$$\epsilon_0\,(1-\epsilon_0^4)^{\frac{1}{4}} = \frac{8}{11}\,\epsilon^{-17} \quad \epsilon_0^4 \sim \epsilon^{-68} \text{ or } (1 - v^2/c^2) \sim {}^{-68} \sim 10^{-29}$$

$$(11, 12) \quad i.e., \; \epsilon_0 \sim \epsilon^{-17} \text{ or } v/c \sim 1$$

showing that $y = v/c$ is *very nearly equal to unity*. From equation (11, 10) we can therefore write

$$(11, 13) \quad x = r_0/a \sim 17.$$

This gives an *estimate of the ring-radius*[11] *adequate to explain the mass of the proton.*

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[11] Dr. Beth has kindly written to me about an attempt to determine the value of a for which the energy has a minimum. For this purpose, he takes account of some additional terms which I have omitted in (7, 4) and in place of (7, 5) he takes:

$$E = \frac{4c^2}{a} \cdot \frac{1+z^2}{2} \log\left[\frac{16\pi}{\alpha}\left(\frac{a}{r_0}\right)^2\right].$$

The minimising of E gives rise to a quintic equation which he has solved by a method of approximation, giving

$$a = r_0 \cdot 10^{16 \pm 1,6}$$

a result which, as Prof. Born has pointed out to me in a letter, is of an impossible order of magnitude.

12. Conclusion.

I hope to return in a future paper to the treatment of the ring-singularity in the general case and deal with questions connected with the conservation laws and self force and the equations of motion in a constant external field.

It gives me the greatest pleasure to thank Prof. Max Born for suggesting the problem, constantly guiding and advising me while here and corresponding with me from Cambridge.

A THEOREM ON ACTION FUNCTIONS IN BORN'S FIELD THEORY.

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1. *Introduction.*

Infeld has shown[1] that, in the development of Born's field theory from a variational principle, it is possible to replace the action function originally adopted by Born and Infeld[2] by a more general one T which satisfies the conditions

$$p^{kl} = \frac{\partial T}{\partial f_{kl}} \; ; \; f^{*kl} = \frac{\partial T}{\partial p_{kl}^*} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

Here, T is assumed a function of F, P, R, where

$$F = \tfrac{1}{2} f_{kl} f^{kl} \; ; \; P = \tfrac{1}{2} p_{kl}^* p^{*kl}, \; R = -\tfrac{1}{2} f^*_{kl} p^{*kl} = \tfrac{1}{2} f_{kl} p^{kl} \quad .. \quad (2)$$

and f_{kl} as well as p_{kl}^* are treated as independent variables. We shall call action functions satisfying conditions (1) *self-conjugate action functions.*

Infeld has deduced the necessary and sufficient conditions for an action function being self-conjugate and used these conditions to obtain a new action function which leads, in the static case, to two solutions with central symmetry one giving a finite, the other an infinite energy. There is however a fundamental difference between Infeld's action function and the Lagrangian used by Born and Infeld in that while the latter is derived from considerations of relativistic invariance the former is not.

In trying to construct action functions which satisfy both the conditions of self-conjugacy and relativistic invariance, I have come to the conclusion that there are no such functions other than Born's action function. I have been thus led to prove in this paper the

Theorem :—*The only self-conjugate action function which satisfies the condition of relativistic invariance is Born's action function.*

2. *Infeld's Conditions for Self-Conjugate Action Functions.*

Infeld has shown that the condition of T being self-conjugate and the assumption that T = Lagrangian + Hamiltonian are entirely equivalent.

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[1] Infeld, *Proc. Camb. Phil. Soc.*, 1936, **32**, Part I, p. 127.

[2] Born and Infeld, *Proc. Roy. Soc.*, A, 1934, **144**, 425.

Another form of the conditions he has deduced is that of the equations

$$R = T_F \cdot F - T_P \cdot P \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

$$R^2 = -FP \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

$$T_F \cdot F + T_P \cdot P + T_R \cdot R = 0 \quad .. \quad .. \quad .. \quad .. \quad (5)$$

the independence of *only two* is a necessary and sufficient condition for T being self-conjugate. This is always the case if T can be represented as a homogeneous function of F, P, R of zero degree. In this case, (5) is identically satisfied and the other two determine F and R as functions of P.

3. *Born's Action Function.*

In the form given by Infeld, Born's action function is

$$T = \frac{F - P}{R} - 2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (6)$$

This satisfies the condition (5) and also the condition that in the limiting case for $f_{kl} = p_{kl}$ and when f_{kl} and p_{ki} are very small, T is equal to zero as it ought to be since in this case the Maxwellian field equations represent the limiting case for very weak fields.

We shall derive the form (6) so as to bring out explicitly the notion of relativistic invariance. The variation principle of least action is to be used in the form

$$\delta \int T d\tau = 0 \quad (d\tau = dx^1 dx^2 dx^3 dx^4) \quad .. \quad .. \quad .. \quad .. \quad (7)$$

and T is to be found from the postulate that the *action integral has to be an invariant*. In this case, the field is determined by the two covariant tensors a_{kl} and b_{kl} which could be split up into symmetrical and antisymmetrical parts by

$$\left.\begin{aligned} a_{kl} &= g_{kl} + f_{kl}\,;\; b_{kl} = g_{kl} + p_{kl}^* \\ g_{kl} &= g_{lk}\,;\; f_{kl} = -f_{lk}\,;\; p_{kl}^* = -p_{lk}^* \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (8)$$

The reason for assuming that the field is determined by two covariant tensors is that, in consonance with Infeld, we assume f_{kl} and p_{kl}^* to be independent variables. The invariance of the action-integral leads to the condition that T should be any homogeneous function of the determinants of the covariant tensors of order $\frac{1}{2}$[3]. We have the expressions

$$\sqrt{-|g_{kl}+f_{kl}|},\ \sqrt{-|g_{kl}+p_{kl}^*|}\,;\ \sqrt{-|g_{kl}|},\ \sqrt{|f_{kl}|}\,;\ \sqrt{|p_{kl}^*|}\,. \quad (9)$$

which multiplied by $d\tau$ are invariant, where the minus sign is added in order to get real values of the square roots.

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[3] Born and Infeld, *Proc. Roy. Soc.*, A, 1934, **144**, 429.

The simplest homogeneous function of degree $\frac{1}{2}$ which we can form out of the expressions (9) is the linear expression

$$T = \sqrt{-|g_{kl}+f_{kl}|} + A\sqrt{-|g_{kl}+p_{kl}^*|} + B\sqrt{-|g_{kl}|} + C\sqrt{|f_{kl}|} + D\sqrt{|p_{kl}^*|} \quad .. \quad (10)$$

Assuming that f_{kl} and p_{kl} are rotations of potential vectors, we can take $C = 0$, $D = 0$. Further A and B are determined by the condition that in the limiting case of Cartesian Co-ordinates and weak fields, T must reduce to $\frac{1}{2}(F + P)$ so that T may be equal to zero for $p_{kl} = f_{kl}$.

Now,

$$\left.\begin{aligned} -|g_{kl}+f_{kl}| &= 1 + F - |f_{kl}| = 1 + F - G^2 \\ -|g_{kl}+p_{kl}^*| &= 1 + P - |p_{kl}^*| = 1 + P - Q^2 \end{aligned}\right\} \quad .. \quad (11)$$

where $G = \frac{1}{4} f_{kl} f^{*kl}$, and $Q = \frac{1}{4} p^{kl} p_{kl}^*$

For small values of f_{kl} and p_{kl}^* the last determinants on the right-hand sides of the first two expressions of (11) can be neglected and (10) becomes equal to $\frac{1}{2}(F + P)$ only if $A = 1$, and $B = -2$. Hence (10) reduces to

$$T = \sqrt{1+F} + \sqrt{1+P} - 2 \quad .. \quad .. \quad .. \quad .. \quad (12)^4$$

where, for the sake of simplicity, we have neglected G and Q, thus assuming that T depends only on F and P.

Applying equations (3) and (5) to (12), we have

$$R = \frac{F}{2\sqrt{1+F}} - \frac{P}{2\sqrt{1+P}} \quad .. \quad .. \quad .. \quad .. \quad (13)$$

$$0 = \frac{F}{2\sqrt{1+F}} + \frac{P}{2\sqrt{1+P}} \quad .. \quad .. \quad .. \quad .. \quad (14)$$

From (13) and (14) we get

$$\sqrt{1+F} = \frac{F}{R}, \text{ and } \sqrt{1+P} = -\frac{P}{R}$$

and (12) reduces to

$$T = \frac{F-P}{R} - 2$$

which is expression (6). This derivation shows that Born's T is self-conjugate and makes the action integral relativistic invariant.

4. *Proof of the Theorem.*

Instead of the linear expression (10) let us consider the general homogeneous function of degree $\frac{1}{2}$ which can be formed out of $-|g_{kl}+f_{kl}|$;

[4] This form of (12) is an immediate deduction from Infeld's theorem that T is to be the sum of a Lagrangian and a Hamiltonian for T being self-conjugate.

$-|g_{kl}+p_{kl}^*|$ and $-|g_{kl}|$, neglecting again the dependence of T on the invariants G and Q. We have, therefore, to form the general homogeneous function of order unity in the variables

$$\sqrt{-|g_{kl}+f_{kl}|},\ \sqrt{-|g_{kl}+p_{kl}^*|} \text{ and } \sqrt{-|g_{kl}|}$$

Since the third term is a numerical invariant equal to unity, such a general function can be written, using (11), in the form

$$T = f(\sqrt{1+F},\ \sqrt{1+P}) + A\sqrt{-|g_{kl}|} \quad .. \quad .. \quad (15)$$

where f *is a homogeneous function of order unity in* $\sqrt{1+F}$ and $\sqrt{1+P}$. Putting $\sqrt{1+F}=\alpha$, and $\sqrt{1+P}=\beta$, (15) can be written as

$$T = f(\alpha, \beta) + A \quad .. \quad .. \quad .. \quad .. \quad .. \quad (16)$$

The constant A in (16) is to be determined from the condition that in the limiting case of weak fields $T \to \frac{1}{2}(F+P)$. Writing

$$f(\alpha, \beta) = \phi(F, P),$$

$$\phi(F, P) = \phi(0, 0) + \left\{F\left(\frac{\partial\phi}{\partial F}\right)_{0,0} + P\left(\frac{\partial\phi}{\partial P}\right)_{0,0}\right\} + \text{etc.}$$

$$= f(1, 1) + \left\{F\left(\frac{\partial f}{\partial\alpha}\right)_{1,1}\left(\frac{\partial\alpha}{\partial F}\right)_{0,0} + P\left(\frac{\partial f}{\partial\beta}\right)_{1,1}\left(\frac{\partial\beta}{\partial P}\right)_{0,0}\right\} + \text{etc.}$$

$$= f(1,1) + \tfrac{1}{2}\left\{F\left(\frac{\partial f}{\partial\alpha}\right)_{1,1} + P\left(\frac{\partial f}{\partial\beta}\right)_{1,1}\right\} + \quad .. \quad .. \quad (17)$$

Since $f(\alpha, \beta)$ is homogeneous of order one in α and β

$$\alpha\frac{\partial f}{\partial\alpha} + \beta\frac{\partial f}{\partial\beta} = f \quad .. \quad .. \quad .. \quad .. \quad .. \quad (18)$$

$$\therefore \quad \left(\frac{\partial f}{\partial\alpha}\right)_{1,1} + \left(\frac{\partial f}{\partial\beta}\right)_{1,1} = f(1,1) \quad .. \quad .. \quad .. \quad .. \quad (19)$$

In order that $T \to \frac{1}{2}(F+P)$ as α and $\beta \to 1$, (17) shows that

$$\left(\frac{\partial f}{\partial\alpha}\right)_{1,1} = \left(\frac{\partial f}{\partial\beta}\right)_{1,1} = 1$$

and this gives, taking (19) into consideration

$$f(1, 1) = 2$$

and therefore $A = -2$. Thus the general action function satisfying the condition of relativistic invariance and the limiting condition of reduction to the Maxwellian case is

$$T = f(\alpha, \beta) - 2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (20)$$

We will now determine the form of f by applying Infeld's conditions for being self-conjugate. From the equations (3) and (5)

$$\left.\begin{aligned} R &= T_F \cdot F - T_P \cdot P \\ 0 &= T_F \cdot F + T_P \cdot P \end{aligned}\right\}$$

or

$$2T_P = \frac{R}{F}$$

and

$$2T_P = -\frac{R}{P} \qquad \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ (21)$$

$$f_\alpha = T_\alpha = T_P \cdot \frac{\partial F}{\partial \alpha} = T_P \cdot 2\alpha$$

$$f_\beta = T_\beta = T_P \cdot \frac{\partial P}{\partial \beta} = T_P \cdot 2\beta \qquad \text{since } \alpha = \sqrt{1 + F},\ \beta = \sqrt{1 + P}$$

Hence from (21),

$$f_\alpha = \frac{R}{F}\alpha$$

and

$$f_\beta = -\frac{R}{P}\beta$$

Substituting these values of f_α and f_β in equation (18) *viz.*,

$$\alpha f_\alpha + \beta f_\beta = f(\alpha, \beta)$$

which is valid on account of the homogeneity of f, we get

$$f(\alpha, \beta) = \frac{R}{F}\alpha^2 - \frac{R}{F}\beta^2$$

$$= \frac{R(1 + F)}{F} - \frac{R(1 + P)}{P}$$

$$= \frac{R}{FP}\left\{P(1 + F) - F(1 + P)\right\}$$

$$= \frac{R(P - F)}{FP}$$

Using, now, the relation (4), the right-hand side becomes $(F - P)/R$.

$$\therefore\ f(\alpha, \beta) = \frac{F - P}{R}$$ and (20) reduces to

$$T = \frac{F - P}{R} - 2$$

which is the same as Born's action function (6). We have, therefore, proved the theorem enunciated in § 1.

5. *Conclusion.*

I wish to thank Prof. Max Born for suggesting this problem during the course of his lectures on the new field theory which I had the privilege of attending last year at the Indian Institute of Science, Bangalore.

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